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THE ACTION OF NITROGEN ON WATER VAPOR AT HIGH TEMPERATURES.

BY O. F. TOWER.

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THAT nitrogen unites with oxygen at high temperatures has been known for a long time. Recently, the equilibrium between these gases has been studied by Nernst, who has shown that the reaction follows the law of mass action. He passed air through an iridium tube heated to about 1800°, and determined the quantity of nitric oxide formed.[1] The percentage of gas converted into nitric oxide at certain absolute temperatures and at atmospheric pressure is given in Table I.

TABLE I.

T.	NO formed. Per cent.
1500	0.10
2000	0.61
2500	1.79
3000	3.60

Nernst and von Wartenberg[2] have also recently shown that the dissociation of water vapor at high temperatures into hydrogen and oxygen takes place quantitatively, according to the following thermodynamical equation:

[1] *Nachrichten Kgl. Ges. Wiss.*, Göttingen, 1904, Heft 4.
[2] *Ibid.*, 1905, Heft 1.

$$\log \frac{2x_1^3}{\left(2+\frac{x_1}{100}\right)\left(1-\frac{x_1}{100}\right)^2} =$$

$$11.51 - \frac{25030}{T} + 2.65 \log \frac{T}{1000} - 0.00055\,(T - 1000).$$

T indicates the absolute temperature and x_1 the percentage of dissociation. The degrees of dissociation at a few temperatures and atmospheric pressure as calculated from the above equation are given in Table II.

TABLE II.

T.	Water dissociated. Per cent.
1000	0.000031
1500	0.022
2000	0.561
2500	3.43
3000	12.9

The equations for these two reactions are:

$$N_2 + O_2 = 2NO, \tag{1}$$

and

$$2H_2O = 2H_2 + O_2. \tag{2}$$

The sum of these two equations gives

$$N_2 + 2H_2O = 2NO + 2H_2, \tag{3}$$

which shows that nitrogen must react on water vapor at high temperatures to a certain extent.[1] The constants of the first two reactions at equilibrium can be calculated from the values of Tables I and II for 2000° C. (2273° abs.) and are as follows:

$$\frac{[NO]^2}{[N_2][O_2]} = K_1 = 8.5.10^{-4};^2$$

$$\frac{[H_2]^2[O_2]}{[H_2O]^2} = K_2 = \frac{P}{RT} \times 2.9 \times 10^{-6}.$$

The product of these two equations gives the condition of equilibrium of the third reaction at the same temperature, *viz.*:

$$\frac{[NO]^2[H_2]^2}{[N_2][H_2O]^2} = K_1K_2 = K = \frac{P}{RT} \times 2.5 \times 10^{-9}. \tag{4}$$

To calculate the completeness of the reaction, assume a gaseous mixture three-fourths of which is nitrogen and one-fourth water vapor, and let the total concentration before the reaction be repre-

[1] A suggestion of this is to be found in the Dissertation of Löwenstein, Göttingen, 1905.

[2] This nomenclature is used to indicate the concentrations of the bracketed substances.

sented by 1. Also let x represent the amount of nitric oxide formed. Then the total concentration after the reaction will be $1+\frac{x}{2}$, and the concentrations of the different gases will be the following:

$$[NO]=[H_2]=\frac{P}{RT}\cdot\frac{x}{1+\frac{x}{2}}=\frac{P}{RT}\cdot\frac{2x}{2+x},$$

$$[N_2]=\frac{P}{RT}\cdot\frac{0.75-\frac{x}{2}}{1+\frac{x}{2}}=\frac{P}{RT}\cdot\frac{1.5-x}{2+x},$$

$$[H_2O]=\frac{P}{RT}\cdot\frac{0.25-x}{1+\frac{x}{2}}=\frac{P}{RT}\cdot\frac{0.5-2x}{2+x}.$$

Substituting these values in equation (4), we have

$$\frac{P}{RT}\cdot\frac{16x^4}{(2+x)(1.5-x)(0.5-2x)^2}=\frac{P}{RT}\times 2.5\times 10^{-9}. \qquad (5)$$

In the denominator x is so small compared with the other numbers that it can be neglected without sensible error. We, therefore, obtain

$$x=0.0033,$$

which means that theoretically 0.33 per cent. of the gaseous mixture can be converted into nitric oxide. Similar calculation for 3000° C. gives 1.5 per cent. for the amount of nitric oxide formed.

QUALITATIVE EXPERIMENTS.

The first experiments were made simply to see whether nitric oxide could be obtained in measurable quantity, and if so, whether it was accompanied by an equivalent quantity of hydrogen.

The nitrogen for all the experiments was prepared by heating a solution of ammonium sulphate and potassium nitrite. The gas was collected in a gasometer and was purified just before use by passing it through sulphuric acid and over glowing copper.

The method employed for detecting nitric oxide was that of Lunge, and consisted in admitting oxygen to the mixed gases, thus converting nitric oxide into nitrogen peroxide, which latter was absorbed by sulphuric acid. The sulphuric acid was afterwards shaken with mercury in a Lunge eudiometer. This lib-

erated nitric oxide, the volume of which could thus be easily determined. Sulphuric acid of 85 per cent. strength was used for this purpose, as nitric oxide is not appreciably soluble in acid of this concentration.

A mixture of nitrogen and water vapor was first passed over a Nernst light, but no appreciable quantity of nitric oxide was obtained. The temperature in this case was about 2000°. The failure to obtain nitric oxide was therefore probably due to the fact that only a small fraction of the gas came into contact with the hot body.

The method, which was finally found to yield measurable quantities of nitric oxide, consisted in passing nitrogen and water vapor over a spark gap. The nitrogen was saturated with water vapor by bubbling through water at a given temperature. The mixed gases then passed directly into the spark bulb. This was 3 cm. in diameter and was provided with platinum electrodes, the terminals of which were 0.7 cm.[1] apart. To avoid the condensation of moisture, the bulb and the tubes leading to and from it, were kept warm. Immediately after the bulb came a small Winkler drying-tube containing sulphuric acid. This tube will hereafter be designated as tube i. Next came the oxygen inlet and then a larger Winkler tube with sulphuric acid, tube ii. After this, in some of the experiments, was another sulphuric acid tube, tube iii. The object of tube i was to remove most of the water vapor and also to prevent oxygen from diffusing backwards into the spark bulb, which would otherwise happen, especially when the velocity of the gases was small. Tube ii served to absorb nitrogen peroxide, and tube iii was a check to show whether this absorption was complete.

In these experiments with the spark bulb, hydrogen was also determined in the following manner. The gases from tube iii were passed over hot copper oxide and then through another sulphuric acid drying-tube, tube iv. The copper oxide acted simply as a catalytic agent, for oxygen was already present in sufficient excess to oxidize the hydrogen. From the increase in weight of tube iv the amount of hydrogen could be easily calculated.

The results with this apparatus are given in Table III. The water through which the nitrogen bubbled was kept at 83° during

[1] Sparks across shorter gaps, *e. g.*, 0 4 cm. yielded only traces of nitric oxide.

these experiments. At this temperature water has a vapor-pressure of half an atmosphere. Therefore, the gas entering the spark bulb consisted of equal volumes of nitrogen and water vapor.

TABLE III.

Nitrogen passed through. Liter.	Length of experiment. Hours.	Water found. Mg.	Nitric oxide found. Cc.	Nitric oxide calculated from water. Cc.
1.0	2	2.3	2.4	3.0
1.25	2	1.6	2.1	2.1
0.85	2	3.6	4.1	4.8
1.5	2	3.1	3.8	4.1

Tube iii was used in the first two of these experiments, but as no nitric oxide was found in it, it was not used in Expts. 3 and 4. No nitric oxide was found in tube i in any of the experiments, which shows that the gases entering the spark bulb were free from oxygen. The amounts of nitric oxide found and the amounts calculated from the water agree sufficiently to show that nitric oxide and hydrogen are produced in equivalent quantities, and that the reaction, therefore, follows the equation given above. Since the temperature was unknown in these experiments, we are unable to make any quantitative use of the results. The reaction, however, probably had not reached an equilibrium, for the amounts of nitric oxide do not depend on the quantity of gas passed through, but rather on the steadiness of the sparks. The sparks were steadier in the last two experiments.

QUANTITATIVE EXPERIMENTS.

In order to determine whether the reaction attains the theoretical equilibrium, use was made of an electrically heated iridium tube, which was kindly placed at my disposal for this purpose by Professor Nernst. This tube had been used by Professor Nernst for similar experiments and reference is made to his papers for further details.[1]

The iridium tube occupied the position of the spark bulb of the preceding experiments. Its temperature, which was maintained at about 2000°, was determined by observation of the interior by means of a Wanner pyrometer immediately before and after each experiment. The mean of these two readings was considered to be the temperature of the experiment. In

[1] *Z. Elektrochem.*, 1903, 623; also *Nachrichten Kgl. Wiss.*, Göttingen, 1904, Heft 4; and also a paper of Jellinck soon to appear in *Z anorg. Chem.*

these experiments the water through which the nitrogen bubbled was kept at 66° so that the gases entering the iridium tube were in the ratio of 3 volumes of nitrogen to 1 volume of water vapor. The results of the experiments are shown in Table IV.

TABLE IV.

Expt. No.	Temp. °C.	Length of experiment. Hours	Nitrogen passed through. Liter.	Total gas volume N_2+H_2O. Liter.	Liter per hour.	Nitric oxide found. I. Cc.	II. Cc.	I+II. Cc.	Per hour. Cc.
1	2009	1.07	2.00	2.67	2.50	0.00	0.50	0.50	0.47
2	2000	1.02	0.7	0.93	0.91	0.22	0.48	0.70	0.69
3	1978	1.50	0.45	0.60	0.40	1.60	1.32	2.92	1.95
4	1987	1.50	0.40	0.53	0.35	0.72	0.69	1.41	0.94
5	1974	0.97	1.55	2.07	2.13	0.14	1.18	1.32	1.36

Under "Nitric oxide found," I indicates the nitric oxide found in tube i, II that found in tube ii, and I+II the sum of these. It will be observed that these experiments differ strikingly from those with the spark bulb, in that nitric oxide was found in tube i in all except the first experiment. This finds its explanation for the most part in the fact that some hydrogen diffused through the hot iridium tube leaving oxygen in excess, which oxidized part of the nitric oxide to nitrogen peroxide. In addition, in Expts. 2 and 3 a small leak was found in the tube, which may have admitted some air. These experiments are, therefore, less trustworthy, but the quantity of air admitted could not have been great, else all the nitric oxide would have been converted into nitrogen peroxide and absorbed in tube i.

That hydrogen actually does diffuse through hot iridium was shown by passing water vapor through the iridium tube first at 1000° and then at 2000°. The issuing gases were tested for excess of oxygen by exploding with hydrogen in a eudiometer. No diffusion could be detected at 1000°, but at 2000° considerable amounts were obtained, as is shown in Table V.

TABLE V.

Water passed through. Gram.	Length of experiment. Minutes.	Oxygen in excess. Cc.	Water passed through. Gram.	Length of experiment. Minutes.	Oxygen in excess. Cc.
1.00	1.25	0.75	1.10	5.0	1.7
1.00	1.25	0.70	1.35	5.0	2.9
0.95	1.25	0.85	0.80	5.0	1.5
Mean, 0.98	1.25	0.77	1.08	5.0	2.1

The water vapor was passed through at two different speeds. It is seen that the amount of hydrogen which diffuses increases

as the speed of the water vapor diminishes. Since water vapor is about 2 per cent. dissociated at 2000°, 1 gram of water would yield 12 cc. oxygen (room temperature), while the average amount found at the smaller speed was 2.1 cc., about 16 per cent. of the possible quantity. Since the rate at which the gases pass through the iridium tube in the nitrogen water vapor experiments was on an average only about one-twentieth of the slower rate of Table V, the diffusion would be somewhat greater, perhaps 50 or 60 per cent. of the possible quantity. But since only one-fourth of the gas was water vapor, we may estimate the oxygen left in excess under the conditions of the experiment at about 15 per cent. of the possible free amount. This is a sufficient quantity to account for the finding of nitric oxide in tube i, and yet not enough to cause any great displacement of the equilibrium of the reaction. That no nitric oxide was found in this tube in Expt. 1 may be because the speed of the gases was greater in this case.

To find whether the results of Table IV throw any light on the equilibrium of the reaction, Expts. 1, 4 and 5, those during which there was no leak in the apparatus, have been recalculated on the basis of 1 liter of gas. The results are given in Table VI.

TABLE VI.

Number of experiment.	One liter gas passed through in x minutes. x.	NO per liter. Cc.
1	24	0.19
5	28	0.64
4	170	2.66

The reaction, it is seen, proceeds very slowly, owing probably to the inertness of nitrogen and to the small concentration of the oxygen. According to the results of the table, the reaction had not reached equilibrium even in Expt. 4. Extrapolating for infinitely slow passage of the gas, we obtain 4.0 cc., approximately, as the amount of nitric oxide per liter. The theoretical value calculated is 3.3 cc. per liter (see above). The agreement is good, but the value extrapolated is somewhat uncertain both on account of the extrapolation and on account of the diffusion of hydrogen through hot iridium.

The reaction here investigated is interesting, chemically, because it shows that water is reduced by nitrogen at high temperatures. The reduction can be increased at will by increasing the quantity of nitrogen.

This research was undertaken at the suggestion of Professor Nernst, and it is a pleasure to express my gratefulness for his help and constant interest in the work. I am also indebted to Dr. von Wartenberg for the results on the diffusion of hydrogen through iridium.

PHYSICAL-CHEMICAL INSTITUTE OF THE UNIVERSITY OF BERLIN,
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COLUMBATES.[1]

BY M. HUME BEDFORD.

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AN EXAMINATION of the literature relating to the columbates of the alkali metals shows decided variations in the ratios existing between the base and the acid. For example, the following sodium columbates have been recorded:

(1) $Na_2O.Cb_2O_5.6H_2O$ or $9H_2O$ (Rose);
(2) $3Na_2O.2Cb_2O_5.24H_2O$ (Rose);
(3) $3Na_2O.Cb_2O_5$ (Rose);
(4) $4Na_2O.5Cb_2O_5$ (Rose);
(5) $3Na_2O.4Cb_2O_5.21H_2O$ (Hermann).

The first salt was obtained by fusing columbic oxide with sodium hydroxide in a silver crucible. Rose pronounced it the best crystallized and most stable of the columbates. The second salt was obtained simultaneously.

When columbic oxide was fused for some time with sodium carbonate the third salt was formed. The fourth salt was described as the only acid salt of exact ratio, while Hermann obtained the fifth salt upon the addition of an excess of sodium hydroxide to a solution of potassium columbium oxyfluoride.

It was resolved, having an abundance of the latter compound, to repeat Hermann's experiment. Accordingly, 50 grams of potassium columbium oxyfluoride were dissolved in a liter of hot water and to this solution a concentrated solution of 150 grams of sodium hydroxide was added. A white, finely divided precipitate separated. It was filtered out and washed with cold water until the filtrate became milky. It was then dried as far as possible by suction and was recrystallized three times from dis-

[1] From the author's thesis for the Ph.D. degree.

tilled water. It was then allowed to dry in the air. It was very stable. It dissolved in water without leaving any residue. Beautiful crystals were obtained when its solution was allowed to cool slowly, but it was found advisable to cool rapidly and stir well because the salt readily formed supersaturated solutions.

On proceeding to the analysis of this compound its water content was obtained by the ignition of a weighed portion of the salt. The ignited sample was then fused with from four to five parts of potassium acid sulphate. The cold melt was boiled with water until it had completely disintegrated, when the columbic oxide was filtered out, thoroughly washed, ignited and weighed. The determination of the sodium content was made by dissolving a portion of the salt in 100 cc. of water, adding from five to ten drops of dilute sulphuric acid and boiling for several minutes, whereupon the columbic hydroxide separated completely, was filtered, washed with boiling water, dried, ignited and weighed as oxide. The filtrate from the columbic hydroxide was evaporated to dryness and the residual sodium sulphate weighed after ignition. A trace of the columbic oxide sometimes remained with the sodium sulphate, which was removed by dissolving the sulphate in water and again filtering. The percentages found for the several constituents were: Na_2O, 16.59 and 16.57; Cb_2O_5, 61.54 and 61.64; H_2O, 21.96 and 22.08, which would lead to the formula $7Na_2O.6Cb_2O_5.32H_2O$, the requirements for which would be Na_2O 16.58, Cb_2O_5 61.42 and H_2O 21.96. These results are far more concordant than those which led Hermann to write the formula as indicated under the fifth salt.

Thinking that possibly the above salt might contain an extra molecule of sodium oxide, its aqueous solution was precipitated by alcohol. The product, after drying, was analyzed and showed the same composition as before, with the exception of the water content, which was now 31 instead of 32 molecules. Hence it may be concluded that the ratio given above correctly represents the composition of the salt.

On adding a dilute solution of barium chloride to a hot solution of the sodium salt, a heavy white precipitate was produced and settled very quickly. It was washed by decantation with boiling water and was then collected on a filter and dried at a water-bath temperature for one and one-half hours, after which it was reduced to a fine powder and analyzed. In its analysis the water content

was obtained by the loss on ignition of a weighed sample. The ignited residue was then fused with a mixture consisting of equal parts of sodium and potassium carbonates. The cold fusion was treated with dilute oxalic acid and hydrochloric acid. Everything dissolved. The liquid was brought to boiling and the barium precipitated in the form of sulphate. The columbium hydroxide was obtained in the filtrate from the barium sulphate. The found percentages of the constituents present were as follows: BaO, 35.83 and 36.08; Cb_2O_5, 53.37 and 53.06; H_2O, 10.80 and 10.75, which led to the formula $7BaO.6Cb_2O_5.18H_2O$, the requirements of which would be BaO 35.66, Cb_2O_5 53.55 and H_2O 10.79. In other words, in this salt again the ratio of the basic oxide and acid oxide remained 7 : 6.

The silver salt was also prepared by treating a solution of the sodium salt with a dilute solution of silver nitrate. It was a white, insoluble precipitate. It was washed by decantation with boiling water, and when dry it was analyzed.

In determining the water a sample of the salt was ignited in a current of dry air and the water collected in a weighed calcium chloride tube. For the estimation of the silver and columbium a second portion of the salt was fused with acid potassium sulphate. The melt was dissolved in boiling water and the columbium determined in the usual way. The silver, contained in the filtrate from the columbium hydroxide, was titrated with potassium sulphocyanate. The percentages of the constituents present were found to be as follows: Ag_2O, 48.72; Cb_2O_5, 48.72; H_2O, 2.52, from which was deduced the formula $7Ag_2O.6Cb_2O_5.5H_2O$, which would require Ag_2O 48.89, Cb_2O_5 48.40 and H_2O 2.71.

Rose described a silver columbate which, according to Rammelsberg, contained Cb_2O_5 50.45, Ag_2O 47.31 and H_2O 1.98.

It was thought that it would be well to prepare a zinc salt, which was done by transposing sodium columbate with zinc sulphate. This salt was white in color and insoluble in water. It was washed by decantation with boiling water and after drying was analyzed. It showed the presence of ZnO 21.86, Cb_2O_5 60.87, H_2O 17.27, from which was deduced the formula $7ZnO.6Cb_2O_5.25H_2O$, requiring ZnO 21.69, Cb_2O_5 61.18 and H_2O 17.13.

The analyses of the four salts described in the preceding paragraphs demonstrate very conclusively that the latter are not derivatives of a metacolumbic acid. On turning to the first

paragraph in this communication it will be observed that the first salt described by Rose shows a ratio favoring the existence of metacolumbates, but the very excellent concordance of the experimental results, as exhibited above, would argue for the ratios which have been deduced. Zinc metacolumbate would require ZnO 19.32 and Cb_2O_5 63.59, or if we were to adopt another ratio, which has been suggested by the study of the potassium salts, namely, that of 8:7, the percentage of zinc oxide required would be 21.23, while that of columbic oxide would be 61.16. It may be added further that the results obtained in the analysis of the barium salt do not harmonize with the requirements of the ratio 8:7.

Having obtained the preceding results from a sodium salt prepared after the manner of Hermann, it was concluded to make the same salt by the methods employed by Rose. To that end 10 grams of ignited columbic oxide were fused with 40 grams of sodium hydroxide in a silver crucible. The excess of sodium hydroxide was washed out, the sodium columbate filtered by suction, and then crystallized twice from water and analyzed after drying in the air. Exceedingly beautiful crystals of the salt were obtained. They were readily soluble in water. Upon analysis they showed the presence of Na_2O 16.65, Cb_2O_5 61.43, and H_2O 21.98, which was in perfect harmony with the requirements of the formula $7Na_2O.6Cb_2O_5.32H_2O$, while Rose himself found in the salt made in this way Na_2O 15.68 and Cb_2O_5 60.82. If his formula for the metacolumbate in this instance were granted it would require Na_2O 14.16 and Cb_2O_5 61.20.

The second method proposed by Rose consisted in fusing columbic oxide for a long period with sodium carbonate. This gave him the salt $3Na_2O.Cb_2O_5$. In imitation of this experiment 8 grams of columbic oxide were fused in a platinum crucible with 25 grams of sodium carbonate. The cold melt was treated with water, the excess of sodium carbonate washed out and the sodium columbate filtered by suction and then recrystallized from water, in which it dissolved completely. Upon analysis it showed Na_2O 15.84, Cb_2O_5 60.20; and H_2O, 24.16, from which percentages was deduced the formula $7Na_2O.6Cb_2O_5.36H_2O$. The only difference, therefore, between this salt and the sodium salts prepared by the other two methods was a slightly higher percentage of water. There

was a great tendency on the part of the salt to form supersaturated solutions, and in order to obtain it from the same it was necessary to add sodium carbonate. It then separated as an extremely fine powder.

It may be concluded from what has been recorded in the preceding paragraphs that but one sodium columbate is definitely known, and that the three methods which have been employed in the past for its preparation lead to one and the same salt, in which the ratio of basic oxide and acid oxide is 7 : 6, which ratio has been preserved in the barium, silver and zinc salts.

It is altogether probable that when the potassium columbates are subjected to a similar study, the many ratios shown by them will be reduced to one simple ratio. This, however, is a matter for further investigation.

SEPARATION OF COLUMBIC AND TUNGSTIC ACIDS.

This study arose from the great difficulty experienced in trying to separate columbic and tungstic oxides in salts obtained by dissolving moist tungstic oxide in a boiling solution of sodium columbate. The purpose was to form columbotungstates analogous to the phosphotungstates and vanadotungstates. A salt was obtained that crystallized in the same form as the sodium columbate and contained about 22.50 per cent. of tungstic oxide and 43.30 per cent. of columbic oxide. It was crystallized without undergoing any decomposition.

In the separation of the columbic and tungstic acids in this salt, concordant results were not obtained by the usual methods. The first method tried consisted in fusing the sample with a mixture of sodium carbonate and sulphur. It will be sufficient to state here that the results varied within wide limits. Digestion of the ignited sample with a strong solution of sodium hydroxide was next tried but did not prove satisfactory.

One of the thoughts that suggested itself was the precipitation of the columbic oxide with magnesia mixture in an alkaline solution, the usual method of separating phosphoric and tungstic acids. It was soon found that the magnesium columbate could not be weighed as such.

PROCEDURE.

Weighed quantities of the two oxides were fused with potassium carbonate (because the potassium salts are more soluble

than the sodium salts). The melt was taken up in 150 cc. of water. To the potassium carbonate solution an excess of magnesia mixture was added. The precipitate formed was allowed to stand several hours and then filtered. It was washed on the filter five or six times with the precipitant, dried and ignited. After all of the carbon had burned off, the residue was fused with acid potassium sulphate, boiled with water, filtered, washed, ignited and the columbic oxide weighed. The tungstic oxide was obtained by difference.

No. of sample.	Cb_2O_5 taken. Gram.	WO_3 taken. Gram.	Cb_2O_5 found. Gram.	WO_3 by difference. Gram.
1	0.2086	0.0986	0.2078	0.0994
2	0.3218	0.1500	0.3208	0.1510
3	0.5004	0.1000	0.4951	0.1053
4	0.2026	0.1000	0.2032	0.0994
5	0.1503	0.1200	0.1506	0.1197

When this method was applied to a solution containing unknown quantities of columbic and tungstic acids, a solution of mercurous nitrate was added, and then a slight excess of nitric acid. Freshly precipitated mercuric oxide was next introduced and the solution boiled five minutes. As soon as the precipitate had settled it was filtered out and washed with boiling water. It was dried, ignited and the columbic and tungstic oxides weighed together. The two oxides were then separated by the method described above. Very fair results were obtained. They varied 0.3 to 0.5 per cent. from the mean.

From a study of the preceding data it will be seen that this method gives very good results. They were superior to those obtained from a sodium carbonate and sulphur fusion. The method can be carried out in a short time and is very easy to manipulate. It was not tried on a mixture of a trace of tungstic oxide and a large quantity of columbic oxide, but under such conditions very good results might be expected.

This method is probably applicable also in the separation of tantalic and tungstic acids.

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POTASSIUM PERCARBONATE.

By William D. Brown.

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Since Constam and Van Hansen described the method for the manufacture of potassium percarbonate,[1] it has been thought that it would be useful as an oxidizing agent. In the preparation of this compound the method of the above authors was followed rather closely.

Potassium percarbonate is prepared by electrolyzing a saturated solution of the carbonate at a temperature below 0° C. A porous cell of 200 cc. capacity was placed in a cylindrical vessel of such size that the outer or anode space had a capacity of 150 cc. In the porous cell was the cathode of nickel gauze and the cathode solution of 20–40 per cent. potassium carbonate. Around the porous cell, in the concentrated solution of potassium carbonate, a platinum wire was wound as a spiral. The whole was immersed in a mixture of ice and common salt, which brought the temperature down to —15° C.

A concentrated solution of pure potassium carbonate, at 15° C., has a specific gravity of 1.556. On lowering the temperature of this solution no crystallization takes place, but if the salt be impure, if a small quantity of common salt get into the solution, crystallization takes place on lowering the temperature, and, on passing a current, no crystals of potassium percarbonate are formed.

In reactions of this class it is necessary to have a high anode density and low cathode density. This was attained by having the nickel gauze cathode and platinum wire anode. The wire was 0.0345 cm. thick and 48 cm. long, making an anode surface of 0.05 sq. dm. The authors referred to state that an anode density of 60 amperes per sq. dm. should be used. Accordingly, a current of 3 amperes (and about 10 volts) was used. This heated the solution too much, and a mass of bicarbonate was formed. On shortening the wire to 24 cm., and passing a current of 1½ amperes (the density remaining the same) a mass of blue crystals was obtained floating in the anode solution. These were filtered by suction, when the blue color almost entirely disappeared.

Potassium percarbonate in solution behaves like hydrogen

[1] *Z. Elektrochem.*, **3**, 445 (1897).

peroxide. A solution of percarbonate and an alkaline solution of hydrogen peroxide rapidly decompose, and at the same rate, while an acid solution of either does not lose strength on standing open. Moreover, an acid solution of percarbonate bleaches potassium permanganate. The reaction is $5K_2C_2O_6 + 8H_2SO_4 + 2KMnO_4 = 2MnSO_4 + 6K_2SO_4 + 8H_2O + 10CO_2 + 5O_2$. Accordingly, the strength of potassium percarbonate as an oxidizing agent was determined by titrating with permanganate in sulphuric acid solution. By titrating an aliquot part of the solution with hydrochloric acid (using methyl orange), the amount of potassium is obtained, and by comparing these the percentage of percarbonate in a mixture of percarbonate and bicarbonate is found. The product obtained in several experiments contained only from 30-40 per cent. percarbonate, while the authors mentioned state that a product of 80-95 per cent. percarbonate is obtained.

The formation of potassium percarbonate at this temperature, concentration, and anode density is attributed to the separation of K_2CO_3 into K and KCO_3, the KCO_3 uniting with another KCO_3 to form $K_2C_2O_6$.

A half pound of potassium percarbonate was received from Eimer and Amend. It had been rebottled by them from an importation of 10 pounds. The strength of this salt falls far below the normal. Dissolved in water and aliquot parts titrated with hydrochloric acid and permanganate, it showed a strength of 39.5 per cent. percarbonate. The salt is relatively stable, when kept in the dry state. Exposed over sodium hydroxide solution in a desiccator for twenty-four hours, 5 grams lost strength from 39.5 to 13 per cent. In the open air the strength fell in the same time to 21 per cent. In a large bell jar, connected with the air outside by a calcium chloride tube, the strength fell to 35 per cent. It also lost strength at the same rate when powdered and tightly corked in a small vial. The lumps in which it is purchased lose strength less rapidly than when powdered. Also the sample corked lost strength less rapidly than the sample from which we were using.

The similarity of the reactions of the solution of percarbonate and of the solution of hydrogen peroxide has been mentioned. The oxidizing reactions were studied further, a comparison being made with those of sodium peroxide. With a solution of chromium sulphate, sodium peroxide acts quicker than the percar-

bonate. But the greatest difference is shown in the case of their action on manganese sulphate; the peroxide throws down the brown precipitate of manganese dioxide, while percarbonate produces a small quantity of brown precipitate but mostly the light precipitate of manganese carbonate. On addition of sodium hydroxide to this precipitate in suspension, the dioxide is immediately formed. With a lead salt the same reactions occur.

From these reactions it would appear that the carbonate is formed, and this is oxidized slowly by the available oxygen contained in the solution as hydrogen peroxide. These salts were taken as perhaps the hardest to oxidize. The percarbonate readily oxidizes compounds such as ferrous and stannous salts. It will also liberate iodine from hydriodic acid solution.

Ordinarily, as an oxidizing agent sodium peroxide is to be preferred to potassium percarbonate. Moreover, the molecular weights are to be taken into account. The same amount of available oxygen is furnished by two and one-half times the amount of percarbonate as of peroxide.

In conclusion, potassium percarbonate can be produced from the pure carbonate, and is an oxidizing agent, but an oxidation reaction that cannot be caused by sodium peroxide remains to be found.

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VOLUMETRIC METHODS FOR COPPER.

BY G. FERNEKES AND A. A. KOCH.

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IN LOOKING over the various volumetric methods for the determination of copper we found that a comparative study of the volumetric methods for this element had never been systematically taken up. We therefore decided to work over the principal methods for the purpose of ascertaining their scientific as well as their practical value. In each method the quantity of copper was varied, and the effect of interfering elements tried.

Carefully calibrated pipettes, measuring flasks and burettes were used. The copper sulphate for these experiments was prepared by C. A. F. Kahlbaum and was marked chemically pure. It, however, contained a trace of iron. With this copper sulphate several liters were prepared, so that 50 cc. contained approxi-

mately 0.1 gram copper. The solution was made slightly acid with sulphuric acid in order to prevent the precipitation of basic copper sulphate. Fifty cc. of this solution were diluted to 100 cc., 5 cc. nitric acid (sp. gr. 1.4) added, and the solution electrolyzed with a current of 0.3 ampere for six hours. The determinations gave the following results: Found: Cu, 0.0939, 0.0940, 0.0938. Average, 0.0939, which was taken as the exact amount of copper in 50 cc. of the copper sulphate solution.

POTASSIUM CYANIDE METHOD.

Since the method of Parks,[1] the originator of the potassium cyanide method, was published in 1851, numerous articles have appeared criticizing its accuracy. Liebig[2] showed that the quantity of ammonia employed seriously affected the titrations. Then Fresenius and Fleck[3] showed that ammonium salts had a deleterious effect upon the titrations. It was found that both ammonia and ammonium salts increase the quantity of potassium cyanide used. Steinbeck[4] claims that ammonium salts have only a very slight effect upon the titrations and that for practical purposes they are not worth considering. The same author shows that lead does not influence the results, and also gives some data showing the effect of zinc. In the latter instance it is, however, apparent that Steinbeck means to minimize the errors due to zinc, as Dulin[5] showed in a later paper that zinc, when present above 4 per cent., materially affects the titrations. The potassium cyanide method was very much improved by using sodium carbonate instead of ammonia for the purpose of neutralization. This variation was introduced by J. L. Davies,[6] and F. L. Merry, mentioned in the same article, employed tartaric acid to obtain the blue color and dissolve the precipitated copper carbonate. Finally, Fessenden[7] enumerates the errors of the potassium cyanide titration as usually carried out, and also critically discusses the method when sodium carbonate is used for neutralization. He claims excellent results by the latter variation of the method. As will be seen, we have in a great

[1] *Mining Journal* (1851).
[2] *Ann. Chem.* (Liebig), **95**, 118 (1855); and Mohr: *Ibid.*, **94**, 143 (1855).
[3] *Z. anal. Chem.*, **8**, 15 (1869).
[4] *Ibid.*, **8**, 16 (1869).
[5] This Journal, **17**, 346 (1895).
[6] *Chem. News*, **58**, 131.
[7] *Ibid.*, **61**, 253, 283.

measure duplicated and confirmed the results of the above investigators.

In our experiments, the copper sulphate solution was made ammoniacal with a large excess of ammonium hydroxide, the solution diluted to 100 cc. and tenth-normal potassium cyanide solution added until the blue color just disappeared. The quantities of copper sulphate used were 2 cc., 5 cc., 10 cc., 25 cc. and 50 cc., corresponding to 0.0038 gram, 0.0094 gram, 0.0188 gram, 0.0470 gram and 0.0939 gram copper. The quantities of ammonia (sp. gr. 0.905) used were 6 cc., 12 cc. and 18 cc. Further, the effect of ammonium salts and sodium carbonate was tried. In each case the number of cubic centimeters of potassium cyanide solution required to just dispel the blue color is the average of two titrations. The results are computed on the basis of three determinations, made at room temperature with 50 cc. copper sulphate and 6 cc. ammonium hydroxide. The average of these determinations gave 51.6 cc. potassium cyanide equivalent to 0.0939 gram copper or 1 cc. potassium cyanide equivalent to 0.00182 gram copper. The results obtained are as follows:

N/10 POTASSIUM CYANIDE.

1 cc. KCN = 0.00182 gram Cu.

Boiling Temp.

	NH_4OH added. cc.	Copper taken. Gram.	Copper found. Gram.	Diff.
1	6	0.0038	0.0037	−0.0001
2	12	0.0038	0.0050	+0.0012
3	18	0.0038	0.0066	+0.0028
4	6	0.0188	0.0164	−0.0024
5	12	0.0188	0.0193	+0.0004
6	18	0.0188	0.0212	+0.0024
7	6	0.0939	0.0896	−0.0043

17° C.

	NH_4OH added. cc.	Copper taken. Gram.	Copper found. Gram.	Diff.
1	6	0.0038	0.0049	+0.0011
2	12	0.0038	0.0070	+0.0032
3	18	0.0038	0.0084	+0.0046
4	6	0.0188	0.0200	+0.0012
5	12	0.0188	0.0223	+0.0035
6	18	0.0188	0.0227	+0.0039
7	6	0.0939	0.0939	0.0000
8	12	0.0939	0.0970	+0.0031
9	18	0.0939	0.0991	+0.0052

0° C.

	NH_4OH added. cc.	Copper taken. Gram.	Copper found. Gram.	Diff.
1	6	0.0038	0.0056	+0.0018
2	12	0.0038	0.0064	+0.0026
3	18	0.0038	0.0083	+0.0045
4	6	0.0188	0.0209	+0.0011
5	12	0.0188	0.0228	+0.0040
6	18	0.0188	0.0242	+0.0054
7	6	0.0939	0.0981	+0.0042

The results obtained in the above tables vary with the amount of copper in 100 cc. of solution, with the temperature, and with the amount of ammonia. Experiments carried out with a half-normal potassium cyanide solution, which corresponds more nearly to the strength used in practice, gave results which were in accordance with the above tables.

A series of experiments were now carried out for the purpose of determining the effect ammonium salts have upon the titration. Three salts were tried, *viz.*, ammonium chloride, ammonium sulphate and ammonium nitrate. In each case 5 grams of the salt were added before making the titration.

N/2 Potassium Cyanide.

1 cc. = 0.00673 gram Cu.

NH_4Cl.

NH_4OH added. cc.	Copper taken. Gram.	Copper found. Gram.	Diff.
6	0.0939	0.1051	+0.0112

$(NH_4)_2SO_4$.

6	0.0939	0.1110	+0.0171

NH_4NO_3

6	0.0939	0.1062	+0.0123

The three results given in the above table show that ammonium salts considerably increase the amount of potassium cyanide required to dispel the blue color.

The variation introduced by J. L. Davies[1] was now tried. The copper sulphate solution was treated with a slight excess of sodium carbonate, and titrated with potassium cyanide. The precipitated basic copper carbonate gradually disappeared, the solution turned intensely blue and on further addition of potassium cyanide became colorless, the end-point being very distinct. The number of cubic centimeters of potassium cyanide used in three determinations with varying amounts of copper are as follows: (1) 50 cc. $CuSO_4$ solution required 24.03 cc. KCN;

[1] *Chem. News*, **58**, 131.

(2) 25 cc. $CuSO_4$ solution required 7.01 cc. KCN; (3) 5 cc. $CuSO_4$ solution required 1.40 cc. KCN.

The results show that when one-half and one-tenth the amount of copper was contained in the solution, only one-half and one-tenth the number of cubic centimeters of potassium cyanide were used. From the good agreement obtained in the above determinations it appears that the addition of a cubic centimeter of ammonia, after neutralization with sodium carbonate, as suggested by Sutton,[1] is unnecessary. Furthermore an excess of sodium carbonate did not influence the results.

The effect of lead, cadmium, arsenic, antimony and tin salts was tried. Lead salts did not influence the titrations, while cadmium salts seemed to increase the quantity of potassium cyanide used in proportion to the quantity of cadmium salt added. Arsenic, antimony and tin salts in the reduced condition seriously changed the results, but in the oxidized state were without influence on the titrations. The error introduced by using zinc to precipitate the copper from its solutions can be entirely avoided by using aluminum, which we have found does not affect the results.

Our results show, that the quantity of potassium cyanide required to make a titration for copper, decreases with an increase of temperature, but increases with an increase of ammonia or ammonium salts. Further the quantity of potassium cyanide used varies with the quantity of copper in 100 cc. of solution, when ammonia is used for neutralization instead of sodium carbonate. In performing these experiments it was noticed that the quantity of potassium cyanide required to just dispel the blue color, varied with the speed with which the titration was performed, but no definite tests were made as to the extent of this variation. The percentage errors resulting from these differences may be very great when small quantities of copper are to be determined, as is the case with tailings and slags, where the copper is titrated hot after precipitating the iron with ammonia.

That this may really be the case, is shown by the results obtained on a symposium of copper and copper matte, initiated by Dr. A. R. Ledoux[2] of New York City. Six chemists reported results by the cyanide method ranging from 54.80–50.55 per cent.,

[1] Sutton's "Volumetric Analysis," 7th ed., p. 179.

[2] *Trans. A. I. M. E.*, **25**, 250, 1000; Dewey: This Journal, **18**, 814.

all but one being lower than the lowest electrolytic determination. It is, however, probable that good results can be obtained, if the copper in the unknown is titrated under the same conditions as when the potassium cyanide solution is standardized; that is, temperature, dilution, ammonia, ammonium salts, and the time required to perform the titration and standardization must be the same. Otherwise it is better to use sodium carbonate for neutralization instead of ammonia, and then perform the titration with standard potassium cyanide solution.

POTASSIUM IODIDE METHOD.[1]

The solution of copper sulphate was put into an Erlenmeyer flask, any free mineral acid neutralized with ammonia, then made slightly acid with acetic acid, 3 grams potassium iodide added, and the free iodine liberated according to the reaction

$$2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 + 4K(C_2H_3O_2) + 2I,$$

titrated with approximately tenth-normal sodium thiosulphate and starch solution. The sodium thiosulphate solution was standardized with twice resublimed iodine and the copper value for tenth-normal thiosulphate computed. The starch solution was made in the ordinary way and kept in well-stoppered sterilized bottles.[2] In all the experiments given below the dilution was 100 cc.

Low[3] claims that in order to obtain the right amount of copper it is necessary to add at least 3 grams potassium iodide. We have carried out a series of determinations to see if with smaller quantities of copper less potassium iodide could be used, to liberate the equivalent quantity of iodine. Two cc. copper sulphate solution equivalent to 0.0038 gram copper were made up to 100 cc., 2 cc. of acetic acid (80 per cent.) and 0.5 gram potassium iodide added. This solution was allowed to stand ten minutes and frequently shaken. One drop of sodium thiosulphate solution was found sufficient to dispel the blue color. The same experiment was repeated and the solution allowed to stand twelve hours. Again one drop of sodium thiosulphate solution was sufficient to dispel the blue color. In the next two experiments the same quantities of copper sulphate, potassium iodide and acetic acid were used. This solution was shaken frequently for

[1] Low: This Journal, **18**, 457; **24**, 1082; *Eng. Min. J.*, 1896, p. 124.
[2] Treadwell: Kurze's "Lehrb. Analyt. Chem.," B. II., 2te. auf., p. 452.
[3] This Journal, **18**, 457.

ten minutes, then diluted to 100 cc. and titrated. The quantity of tenth-normal thiosulphate used was 0.35 cc. = 0.0022 gram copper and 0.37 cc. = 0.0024 gram copper. The same experiment repeated without the addition of acetic acid required 0.30 cc. tenth-normal thiosulphate = 0.0019 gram copper.

We next varied the quantity of potassium iodide. Two cc. copper sulphate solution and 1.5 grams potassium iodide were diluted to 100 cc., and titrated without the addition of acetic acid. The amount of sodium thiosulphate required was 0.47 cc. = 0.0030 gram copper. The same experiment with the addition of acetic acid and allowing the solution to stand five minutes required 0.55 cc. thiosulphate solution = 0.0035 gram copper. In all the above tests the blue color reappeared upon standing; another drop of thiosulphate solution would again dispel the blue color, but the blue color would continue to return until the equivalent quantity of iodine had been liberated. Using 2 cc. copper sulphate = 0.0038 gram copper, 2 grams potassium iodide and 2 cc. acetic acid, two determinations gave 0.60 cc. and 0.58 cc. tenth-normal thiosulphate = 0.0038 gram copper. In these two cases the solution remained colorless for some time upon standing.

Experiments were now performed with varying quantities of copper sulphate, using 2.5 grams of potassium iodide. The results are as follows:

	Copper taken. Gram.	Copper found. Gram.	Diff.
1	0.0939	0.0936	—0.0003
2	0.0939	0.0938	—0.0001
3	0.0939	0.0937	—0.0002
4	0.0939	0.0941	+0.0002
5	0.0939	0.0940	+0.0001
6	0.0470	0.0470	0.0000
7	0.0470	0.0473	+0.0003
8	0.0188	0.0188	0.0000
9	0.0188	0.0190	+0.0002
10	0.0188	0.0186	—0.0002
11	0.0188	0.0187	—0.0001
12	0.0038	0.0038	0.0000
13	0.0038	0.0038	0.0000
14	0.0038	0.0038	0.0000
15	0.0038	0.0037	—0.0001

In Nos. 4 to 9, 5 cc. acetic acid were added. In No. 14 the potassium iodide was added before making up the solution to 100 cc. In No. 15 the acetic acid was omitted.

Experiments showed that arsenic, antimony and tin salts in the oxidized form, when added to the copper sulphate solution, do not affect the titrations. In the case of arsenic, two tests on 10 cc. copper sulphate = 0.0188 gram copper, and 0.5 gram sodium arsenate, gave 0.0187 gram and 0.0188 gram copper respectively. Similar results were obtained for antimony and tin. The effect of lead, bismuth, cadmium, zinc and aluminum salts was tried, and found to be without influence upon the titrations. In the case of lead and bismuth it was somewhat difficult to tell the end-point of the reaction.

Our results show that an excess of acetic acid does not influence the titrations. In order to correctly determine the amount of copper in a solution of 100 cc. containing 0.0038 gram copper, at least 1.5–2 grams potassium iodide must be added, and for a solution containing 0.0939 gram copper per 100 cc., 2.5 grams potassium iodide are sufficient to liberate the equivalent quantity of iodine.

FERROCYANIDE METHOD.[1]

In this method, the copper sulphate solution, slightly acid with sulphuric acid, was titrated hot with a standard solution of potassium ferrocyanide. The reaction

$$2CuSO_4 + K_4Fe(CN)_6 = Cu_2Fe(CN)_6 + 2K_2SO_4$$

is complete when a drop of the solution brought into contact with a drop of dilute ferric chloride solution on a white porcelain plate gives a blue coloration. The end-point in this reaction, using ferric chloride as an indicator, is indistinct. Near the end-point of the reaction a dirty dark spot is obtained with ferric chloride, which on further addition of potassium ferrocyanide becomes blue. This dirty coloration is evidently due to the brown precipitated cupric ferrocyanide.

At room temperature the precipitate of cupric ferrocyanide is very finely divided, but upon boiling becomes flocculent and settles more rapidly. For the results given below the titrations were performed hot, but it was never possible to free the solution entirely from the fine granular precipitate, and the above-mentioned dirty coloration invariably appeared. The copper value of 1 cc. of the potassium ferrocyanide solution was 0.00427 gram copper. The results were computed from this value.

[1] Matteo Spica: *Staz. Sperim. Agric. ital.*, **26**, 593 (1894); *Chem. Centrbl.*, **65**, 815 (1894).

	Copper taken. Gram.	Copper found. Gram.	Diff.
1	0.0929	0.0931	+0.0002
2	0.0929	0.0927	—0.0002
3	0.0465	0.0453	—0.0012
4	0.0465	0.0452	—0.0013
5	0.0093	0.0088	—0.0005
6	0.0093	0.0092	—0.0001

The following elements are precipitated under similar conditions, by means of potassium ferrocyanide: silver, lead, cadmium, mercury, bismuth, zinc, manganese, nickel, cobalt and iron. It is therefore evident, that this method can only be used with a pure solution of copper.

CUPROUS THIOCYANATE, METHOD OF RIVOT.[1]

Fifty cc. of the copper sulphate solution, slightly acidified with sulphuric acid, were saturated with sulphur dioxide, ammonium thiocyanate added until in slight excess, the solution stirred and the precipitate allowed to settle several hours. Pure white cuprous thiocyanate settled out. The cuprous thiocyanate was then filtered through a previously dried and weighed Gooch crucible, washed until free from ammonium thiocyanate, the crucible with the precipitate dried at 110° C. and again weighed; the difference in the two weighings gave the weight of cuprous thiocyanate. The following are the results:

	$Cu_2(CNS)_2$ Gram.	Copper taken. Gram.	Copper found. Gram.	Diff.
1	0.1800	0.0939	0.0941	+0.0002
2	0.1798	0.0939	0.0939	0.0000
3	0.1798	0.0939	0.0939	0.0000
4	0.0362	0.0188	0.0188	0.0001
5	0.0360	0.0188	0.0188	0.0000

The results obtained with a pure copper sulphate solution show a very close agreement with the theoretical, for both the larger and smaller amounts of copper.

VOLHARD'S METHOD.[2]

In this method the copper is precipitated by a standard potassium thiocyanate solution under the same conditions as described under the method of Rivot. The excess of potassium thiocyanate is titrated by means of a standard silver nitrate solution, using

[1] *C. R.*, **38**, 868; also R. G. Van Name: *Z. anorg. Chem.*, **26**, 230; Busse: *Z. anal. Chem.*, **17**, 53; **30**, 122; Treadwell: Kurze's "Lehrb. Analyt. Chem.," 2te. auf., B. II, p. 126.

[2] *Ann. Chem. Pharm.*, **190**, 251 (1877); *Z. anal. Chem.*, **18**, 285 (1879).

iron alum as an indicator. The assumption is, that no other element excepting silver is precipitated by potassium thiocyanate in acid solution. Chlorides must not be present, but this condition is fulfilled in the course of an ordinary copper assay. A tenth-normal silver nitrate solution was employed, and the potassium thiocyanate solution was standardized against the silver nitrate solution. The results in the table below were obtained with a copper sulphate solution. One cc. potassium thiocyanate was equivalent to 0.006299 gram copper.

	Copper taken. Gram	Copper found. Gram.	Diff.
1	0.0929	0.0926	—0.0003
2	0.0929	0.0925	—0.0004
3	0.0465	0.0463	—0.0002
4	0.0465	0.0461	—0.0004
5	0.0093	0.0093	0.0000
6	0.0093	0.0092	—0.0001

We again tried the influence of various interfering elements, first upon potassium thiocyanate, and then upon silver nitrate. As previously stated, the only other element precipitated by potassium thiocyanate in acid solution is silver. It was, however, found that arsenic in the oxidized state gave a precipitate with silver nitrate, which seriously affected the results, so that this method could not be used with copper ores containing arsenic.

ACIDIMETRIC METHOD.[1]

The copper in the copper sulphate solution was precipitated with ammonium thiocyanate as in Rivot's method, and the cuprous thiocyanate filtered through a Gooch crucible. The crucible containing the cuprous thiocyanate was put into a porcelain dish, 25 cc. normal sodium hydroxide added, and the solution heated until the reaction

$$Cu_2(CNS)_2 + 2NaOH = Cu_2(OH)_2 + 2NaCNS$$

was complete. The cuprous hydroxide was filtered off and the filtrate titrated to neutrality with normal hydrochloric acid, using methyl orange as the indicator. One cc. normal sodium hydroxide = 0.0636 gram copper. Three determinations gave the following results:

	Copper taken. Gram.	Copper found. Gram.	Diff.
1	0.0939	0.0941	+0.0002
2	0.0939	0.0941	+0.0002
3	0.0939	0.0935	—0.0004

[1] Garrigues: This Journal, **19**, 940 (1897).

The three results obtained with a pure copper sulphate solution show a good agreement among themselves, also with the theoretical amount of copper in the solution.

TITRATION OF THIOCYANIC ACID WITH POTASSIUM PERMANGANATE.

Guess[1] precipitates the copper from an acid solution with an alkaline thiocyanate, and then decomposes the cuprous thiocyanate with sodium hydroxide, according to the equation

$$Cu_2(CNS)_2 + 2NaOH = Cu_2(OH)_2 + 2NaCNS.$$

The sodium thiocyanate formed is made acid with sulphuric acid and the free thiocyanic acid titrated with a standard solution of potassium permanganate. According to the equation

$$10HCNS + 12KMnO_4 + 8H_2SO_4 = 6K_2SO_4 + 12MnSO_4 + 10HCN + 8H_2O,$$

the iron factor multiplied by 0.1892 should give the theoretical amount of copper. Guess found that by using 0.192 instead of 0.1892 as the factor, he obtained results which more nearly express the exact amount of copper. As the author does not give any experimental data, we have made a series of determinations with a pure copper sulphate solution, so that the results obtained by this method can be compared with the results obtained by other methods.

Our method of procedure was as follows: After precipitating the copper in the copper sulphate solution according to the method of Rivot, the precipitate was filtered on a Gooch filter and washed until free from ammonium thiocyanate. Then a hot solution of sodium hydroxide was poured through the filter and the cuprous hydroxide washed free from sodium thiocyanate, or the Gooch filter and precipitate were removed to a porcelain dish and then treated with hot sodium hydroxide, the precipitate stirred to insure intimate contact with the sodium hydroxide, then filtered and washed thoroughly. The strength of the sodium hydroxide was varied to see if it in any way altered the results. The sodium thiocyanate was then made decidedly acid with sulphuric acid, and titrated with a standard solution of potassium permanganate.

The potassium permanganate solution was carefully stand-

[1] This Journal, **24**, 208.

ardized against ferrous ammonium sulphate and the copper value computed by multiplying the iron value by 0.192.

1 cc. $KMnO_4$ = 0.005448 gram iron

or

1 cc. $KMnO_4$ = 0.001046 gram copper.

The following results were obtained by this method.

	Strength of NaOH to decompose $Cu_2(CNS)_2$. Per cent.	Copper taken. Gram.	Copper found. Gram.	Diff.
1	10	0.0939	0.0925	—0.0004
2	10	0.0939	0.0942	+0.0002
3	10	0.0939	0.0935	—0.0004
4	10	0.0939	0.0930	—0.0009
5	2	0.0939	0.0929	—0.0010
6	2	0.0939	0.0931	—0.0008
7	2	0.0939	0.0930	—0.0009
8	1	0.0929	0.0920	—0.0009
9	1	0.0929	0.0922	—0.0007
10	1	0.0465	0.0459	—0.0006
11	1	0.0465	0.0459	—0.0006
12	10	0.0188	0.0173	—0.0015
13	10	0.0188	0.0173	—0.0015
14	10	0.0188	0.0176	—0.0012

With a single exception our results are lower than the theoretical values, although we used the higher factor 0.192 instead of the factor 0.1892 computed from the equation given above.

TITRATION OF THE IRON EQUIVALENT OF COPPER BY MEANS OF POTASSIUM PERMANGANATE.

According to Meade[1] the copper is again precipitated as cuprous thiocyanate, and treated with sodium hydroxide as in the previous method. The cuprous hydroxide is then dissolved in a dilute sulphuric acid solution of ferric chloride or ferric sulphate, the cuprous hydroxide dissolving, and reducing a corresponding amount of iron from the ferric to the ferrous state.

$$Cu_2(OH)_2 + Fe_2(SO_4)_3 + H_2SO_4 = 2CuSO_4 + 2FeSO_4 + 2H_2O.$$

The ferrous sulphate is then titrated with a standard solution of potassium permanganate. According to the author the iron value of the permanganate used, multiplied by 1.125, gives the amount of copper.

We precipitated the copper with ammonium thiocyanate and decomposed the cuprous thiocyanate with sodium hydroxide as

[1] This Journal, **20**, 610.

before. Various strengths of sodium hydroxide, both hot and cold, were used to decompose the cuprous thiocyanate. The cuprous hydroxide was then dissolved in a solution of ferric chloride, or ferric sulphate containing a little sulphuric acid, care being taken to have the iron salt in large excess. The Gooch crucible containing the cuprous hydroxide was either put into a porcelain dish, the dissolving solution added, and the dish warmed and stirred until the cuprous hydroxide had gone into solution and then filtered; or, the warm dissolving solution was poured through the Gooch crucible. In each case a little sodium carbonate, and dilute sulphuric acid were put into the flask into which the solution of reduced ferric salt was to be filtered. In this way sufficient carbon dioxide was generated to expel the air from the flask, and prevent any oxidation of the ferrous iron by the oxygen of the air. The reduced ferric chloride, or ferric sulphate solution was then titrated with a standard solution of potassium permanganate and the amount of copper calculated.

Meade multiplies the iron value of the permanganate by 1.125 to obtain the copper value. From the equation

$$Cu_2(OH)_2 + Fe_2(SO_4)_3 + H_2SO_4 = 2CuSO_4 + 2FeSO_4 + 2H_2O,$$

this would mean Fe : Cu as 56.63. Taking the atomic weight of Fe = 55.9 and Cu = 63.6, as given in the table of international atomic weights for 1905, we would obtain a factor which equals 1.138. In our determinations the results have been computed separately for each factor, as the following tables show.

	Strength of NaOH used to decompose $Cu_2(CNS)_2$. Per cent.	Copper taken. Gram.	F=1.125 Copper found. Gram.	Diff.	F=1.128 Copper found. Gram.	Diff.
1	2–4	0.0939	0.0843	—0.0096	0.0852	—0.0087
2	2–4	0.0939	0.0873	—0.0066	0.0883	—0.0056
3	2–4	0.0939	0.0742	—0.0197	0.0750	—0.0189
4	2–4	0.0939	0.0674	—0.0265	0.0682	—0.0257
5	2–4	0.0939	0.0742	—0.0197	0.0750	—0.0189
6	2	0.0939	0.0674	—0.0265	0.0682	—0.0257
7	2	0.0939	0.0803	—0.0136	0.0812	—0.0127
8	10	0.0939	0.0631	—0.0308	0.0638	—0.0301
9	10	0.0939	0.0592	—0.0347	0.0599	—0.0340

Nos. 1 and 2 were dissolved in a solution of 1 gram ferric ammonium sulphate, 25 cc. distilled water and a little sulphuric acid.

Nos. 3 to 9 were dissolved in a solution of 0.5 gram ferric chloride, 25 cc. distilled water and a little sulphuric acid.

In No. 6 the cuprous thiocyanate was decomposed with sodium hydroxide at room temperature. In the other eight determinations, hot sodium hydroxide was used for the decomposition of the cuprous thiocyanate.

It is clear that the low results given in the above table are not due to the difference in the value of the factor, but are due to some other cause. It was noticed that the cuprous hydroxide, after the treatment with sodium hydroxide solution, often appeared quite black on the surface, probably due to a slight oxidation by the hot sodium hydroxide solution. In No. 6, sodium hydroxide at room temperature was used to decompose the cuprous thiocyanate; while the cuprous hydroxide did not blacken as much as in the other tests, where hot sodium hydroxide was used, no better result was obtained. The asbestos in the Gooch crucible was then treated with nitric acid and found to contain considerable copper, but by no means enough to make up the theoretical amount of copper taken. We next tried a larger excess of ferric salt. The following are the results obtained:

	Strength of NaOH used to decompose $Cu_2(CNS)_2$. Per cent.	Copper taken. Gram.	F=1.125. Copper found. Gram.	Diff.	F=1.138. Copper found. Gram.	Diff.
10	10	0.0929	0.0925	—0.0004	0.0936	+0.0007
11	5	0.0929	0.0956	+0.0027	0.0966	+0.0037
12	10	0.0929	0.0971	+0.0042	0.0983	+0.0054
13	10	0.0929	0.0950	+0.0021	0.0961	+0.0021
14	4	0.0929	0.0968	+0.0039	0.0979	+0.0050
15	4	0.0929	0.0971	+0.0042	0.0983	+0.0054
16	4	0.0929	0.0959	+0.0030	0.0970	+0.0041
17	10	0.0188	0.0180	—0.0008	0.0182	+0.0006
18	10	0.0188	0.0190	+0.0002	0.0192	+0.0004

No. 10 was dissolved in a solution of 2 grams ferric chloride, 25 cc. distilled water and 2 cc. sulphuric acid.

No. 11 was dissolved in a solution of 2.5 grams ferric chloride, 25 cc. distilled water and 4 cc. sulphuric acid.

Nos. 12, 13, 14, 17 and 18 were dissolved in a solution of 2.5 grams ferric chloride, 25 cc. distilled water and 3 cc. sulphuric acid. Before titrating No. 14, 20 cc. of the titrating mixture were added.

Nos. 15 and 16 were dissolved in a solution of 5 grams ferric ammonium sulphate, 25 cc. water and 3 cc. sulphuric acid.

In all the above tests Nos. 10 to 18, the cuprous hydroxide was

dissolved by pouring the acid solution of ferric chloride or sulphate through the Gooch crucible, until all the cuprous hydroxide was dissolved. This procedure was more rapid than to remove the asbestos with the cuprous hydroxide to a dish, dissolve the cuprous hydroxide, and then filter; in the greater number of cases the asbestos was free from copper after this treatment. The ferric chloride and ferric ammonium sulphate used for the above determinations were free from ferrous salts; still the results are too high whether we use the factor 1.125 or 1.138. Believing that the iron value of our permanganate solution was too high, we again restandardized our permanganate solution, but obtained the same results as at first.

Recalculating the six results obtained by Meade,[1] with a copper sulphate solution of known strength, on the basis of F = 1.138, we find his results to be on an average too high by 0.0012 gram, while with F = 1.125 to be on an average too low by 0.0011 gram. We were unable to obtain as concordant results by this method as were desired, either with the copper sulphate solution, or with a chalcopyrite ore.

Taking the average of the seven results, Nos. 10 to 16, and computing the factor by which we would have to multiply the iron value of the permanganate, in order to obtain the theoretical amount of copper, we obtain F = 1.092. While this new factor may approximately express the value for a solution containing a quantity of copper = 0.0929 gram, a smaller or larger amount of copper may require some other factor. In order to determine whether the factor varies with the amount of copper, a series of determinations with smaller and larger amounts of copper will be necessary. At best the method is longer and more painstaking than the previous method of titrating the thiocyanic acid with permanganate, and the results have been less satisfactory.

ANALYSIS OF CHALCOPYRITE.

In each case 0.5 gram of ore was used. It was dissolved and treated by familiar methods employed for copper ores. It might, however, be said that aluminum was used to precipitate the copper from the solution. After thoroughly washing the copper by decantation, it was redissolved in nitric acid. The solution was boiled until the brown fumes disappeared. The solution was diluted,

[1] This Journal, **20**, 613.

ammonium hydroxide was added to alkaline reaction and again boiled. Now we acidified with acetic acid, and allowed the solution to assume the room temperature. Three grams of potassium iodide were added and the liberated iodine titrated with a tenth-normal thiosulphate solution.

In determining the copper as cuprous thiocyanate, according to Rivot, the ore was again decomposed as before. The solution was slightly acid with sulphuric acid and saturated with sulphur dioxide, and the copper precipitated with ammonium thiocyanate. The precipitated cuprous thiocyanate was finally weighed in a Gooch crucible. The two permanganate methods were carried out as previously described when pure copper sulphate was used. The results obtained are as follows:

	Electrolytic.		Iodide.		$Cu_2(CNS)_2$.			$KMnO_4$ of HCNS.		$KMnO_4$ of $Cu_2(OH)_2$.	
	Copper found. Gram.	Copper. Per cent.	Copper found. Gram.	Copper. Per cent.	Found. Gram.	Copper. Gram.	Copper. Per cent.	Copper found. Gram.	Copper. Per cent.	Copper found. Gram.	Copper. Per cent.
1	0.1686	33.72	0.1685	33.70	0.3158	0.1650	33.00	0.1662	33.24	0.1767	35.34
2	0.1685	33.70	0.1682	33.64	0.3176	0.1660	33.20	0.1692	33.84	0.1711	34.22
3	.....	.....	0.1685	33.70	.....	.....	.....	.....	.....	.....	.....

The results in the above table show that the iodide method compares very favorably with the electrolytic method. The three results agree very well among themselves and give an average of 33.68 per cent. copper, as compared with an average of 33.71 per cent. copper by the electrolytic method, a difference of 0.03 per cent. This slight difference is insignificant, and can easily be accounted for in filtering, washing, etc. We found that all the copper is precipitated by the aluminum strip, for neither the ammonia nor hydrogen sulphide test showed any copper in the filtrates of the chalcopyrite ore or the copper sulphate solution. Thorn Smith[1] claims that all the copper is not precipitated by means of aluminum; this may be the case with more complicated ores, containing arsenic, antimony, etc., and which we have not analyzed. As far as we have worked with the iodide method, we find that when one has once mastered the manipulations, it is rapid, and, excluding the item of expense, an excellent method for the determination of copper.

The two results in which the copper was weighed as cuprous thiocyanate gave low results. When, however, the thiocyanic acid was titrated with potassium permanganate, results were

[1] *Eng. Min. J.*, p. 1023, Dec., 1904.

obtained which agree very favorably with those obtained with pure copper sulphate solutions.

In No. 1 of the last method we used as the dissolving solution, a solution of 2.5 grams ferric chloride, 25 cc. distilled water and 3 cc. sulphuric acid, but before titrating added 20 cc. of titrating mixture. In No. 2 the ferric chloride was replaced by ferric sulphate, but no titrating mixture was used. In making the computations the iron factor was multiplied by 1.138 to give the copper value. Recalculating the results, using the factor 1.092, we obtain 33.90 per cent. and 32.84 per cent., or an average of 33.37 per cent. copper,—a result which approximates the results obtained by the other methods.

In nearly all of the above methods, the determinations were carried out by each of us independently. In this way the weak points of the methods were brought out more clearly, and gave us a check on our work.

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THE CAUSTIC SODA METHOD OF DETERMINING MOLYBDENUM IN STEEL.[1]

BY GEORGE AUCHY.

Received August 15, 1905.

THIS method as described by the writer in the *Iron Age*, November 20, 1902, was taken up by Cruger and Miller,[2] tested by them and compared with a method of their own which they suggest and describe, and which differs from the writer's method in that the iron is separated from the molybdenum by hydrogen sulphide instead of by caustic soda. The conclusion that their experiments bring them to is that the caustic soda method gives results that are about 0.30 per cent. too high in steels, and about 2.00 per cent. too high in ferromolybdenums, on account of the formation of a molybdate of iron soluble in caustic soda or ammonia. It seemed to the writer that this conclusion was based on insufficient evidence. It is true that the fact that in their experiments, the caustic soda results are lower than results by their own method as above stated is a

[1] Read at the June Meeting of the Philadelphia Section of the American Chemical Society.

[2] This Journal, **26**, 675.

very significant one, when taken in connection with the other fact that their method always brings good results when tested against standard methods—and they make many such tests. And when in addition to these experiments, the authors test the caustic soda solution of the molybdenum after filtration from the iron, qualitatively with potassium thiocyanate, and find iron present, the evidence in favor of their conclusion would seem to be so strong, that it would hardly occur to one to question its correctness, were it not for a quantitative test that they also make (but to which strangely enough they seem to attach no significance), which not only does not corroborate their opinion that the high results by the caustic soda method are due to some iron going into solution in the caustic soda as a soluble iron molybdate, but absolutely disproves that opinion, and indicates that the iron is simply due to traces mechanically carried through the filter-paper by the strong caustic soda. This experiment was as follows: An iron and molybdenum solution was made up in something like the proportions existing in a ferro-molybdenum, the molybdenum separated from the iron by caustic soda, and the latter then tested quantitatively for iron, after getting rid of the molybdenum with sulphuretted hydrogen. Now, to corroborate their theory that the 2.00 per cent. too high molybdenum results, are due to iron dissolved in the caustic soda as iron molybdate, they should have found in this experiment about 0.0200 gram iron oxide. The amount actually found was only 0.0005 gram, or enough only to make a difference of about 0.05 per cent. in the molybdenum result instead of 2.00 per cent. This result would indicate that the iron found by their qualitative tests with sulphocyanide was simply very minute amounts carried mechanically through the filter-paper by the strong caustic soda. This is something the writer for his part, had always been suspicious of and has habitually used double filters, and moreover carried on the dummy test on drillings of molybdenum-free steel instead of on the reagents simply. Evidently, more work is needed before Cruger and Miller's conclusions can be accepted as proved, and the writer resolved to investigate the point thoroughly. It would seem that the question that results by the caustic soda method are too high (0.30 per cent. in steel, 2.00 per cent. in ferro-molybdenum) by reason of a soluble iron molybdate, could best and easiest be investigated and settled

as follows: Let such weights of ordinary C. P. molybdic acid and of steel drillings free from molybdenum be taken as would together correspond to 0.8 gram of a molybdenum steel, or of a ferro-molybdenum. Ordinary C. P. molybdic acid is, of course, far from pure, but for the purposes of this investigation this does not matter. Nor is it in the least necessary to determine the amount of molybdenum in the molybdic acid used. Then let the molybdenum in this mixture be determined by the caustic soda method, as usual. Then let precisely the same weight of molybdenum trioxide be taken for a second experiment, in which the drillings are omitted, carrying out the caustic soda process on the molybdenum trioxide alone, using the same measuring flasks as were used in the first experiment. Now, if the result in the first experiment (when the drilling is used) comes notably higher than the result by the second experiment (when the molybdenum trioxide alone is used), and if at the same time, a quantitative test in the first experiment shows about 0.0030 gram iron oxide (or 0.0200 gram if the proportions be those of a ferro-molybdenum) in the caustic soda solution along with the molybdenum, then, of course, it is proved that Cruger and Miller are right, and a molybdate of iron soluble in caustic soda makes the molybdenum results by this method too high. But on the other hand, if results by these two experiments agree, and if no iron oxide is found with the molybdenum in solution in the caustic soda, then Cruger and Miller must be in error.

The following tests were made by the writer:

No.	MoO_3 and drillings. Molybdenum, per cent.		MoO_3 alone. Molybdenum, per cent.	
1	8.75	8.695	8.67	8.61
2	8.67		8.50	
3	8.67		8.67	
4	43.25		43.35	

These results do not at all bear out Cruger and Miller's contention. It is seen from the above table that results come no higher than when there is no iron at all present. But although these results do not corroborate Cruger and Miller's theory of a soluble molybdate of iron, still, on the other hand, they cannot be taken as absolutely disproving it, for it is not impossible that some other error might counteract and mask the effect of the soluble iron molybdate. For instance, there may have been a loss of molybdenum through some of it coming down with the

ferric hydroxide precipitate, or there may have been enough iron present as an impurity in the C. P. molybdenum trioxide used in the experiments, to form the same amount of soluble iron molybdate. To conclusively prove or disprove the point, it is obviously necessary to make a quantitative determination of the iron in the caustic soda solution of the molybdenum, after the separation from the bulk of the iron by the caustic soda. The following test was thereupon made. Molybdenum trioxide, and steel drillings in the proportions of a molybdenum steel were mixed, dissolved, and the caustic soda separation made as in the regular method. Then instead of finishing as usual, by reducing with zinc and titrating with permanganate, the caustic soda solution of the molybdenum was quantitatively tested for iron as follows. After strongly acidifying with sulphuric acid, the molybdenum was precipitated by hydrogen sulphide, filtered off, redissolved and reprecipitated, and the combined filtrates from the molybdenum sulphide again precipitated with hydrogen sulphide, and filtered from the molybdenum sulphide washed through in the first operation. The hydrogen sulphide was then boiled off, the solution oxidized by nitric acid, evaporated, the silica separated and the iron precipitated with ammonia. With the iron is precipitated the alumina derived from the caustic soda originally used and from the glass vessels. To free the iron from this, the ignited precipitate was fused with a large excess of sodium carbonate, dissolved in water, filtered, dissolved in acid, precipitated with ammonia, and again fused with sodium carbonate, etc., and a third fusion made, and the iron finally precipitated with ammonia.

From the very start a blank or dummy test was, of course, carried along with the regular test. The iron oxide finally weighed was found to have exactly the same weight in the regular test as in the blank or dummy test, showing that no iron whatever had gone into the caustic soda solution as a soluble iron molybdate, and disproving Cruger and Miller's theory. According to them, about 0.0030 gram of ferric oxide should have been found in this experiment. Actually not a trace was found as just stated. Not satisfied with this experiment, another was made in a sample made up to correspond to ferro-molybdenum in the proportions of iron and molybdenum present. In this last experiment 0.0200 gram iron oxide should have been found if Cruger and Miller's

theory is correct. But as in the first experiment, not a trace was found, the regular test, and the blank or dummy test weighing exactly the same. The question now arises, since the soluble iron molybdate theory proves to be untrue, what then is the real reason that Cruger and Miller obtain so much higher results by the caustic soda method than by their own method, which differs from it only in that the iron is separated from the molybdenum by hydrogen sulphide instead of by caustic soda? Assuming their method to be an accurate one, why does the caustic soda separation of iron from molybdenum give too high results? Or, on the other hand, if the caustic soda separation is accurate, why does the hydrogen sulphide separation give too low results?

To the first of these questions it would be difficult to find an answer, now that the soluble iron molybdate theory has been found inapplicable, but to the second an answer readily suggests itself. It is, that the reason why the hydrogen sulphide separation gives too low results is because some of the molybdenum sulphide is lost in the washing, as, according to the writer's experience, is the case with copper and nickel sulphides. But to this theory the objection at once arises that Cruger and Miller thoroughly tested the accuracy of this method in a long series of experiments, in which results by their method agree well with results by the lead molybdate method of Chatard, and by the electrolytic method of Smith and Kollock. But to this objection also a reply may be found. Cruger and Miller standardized their permanganate solution by ferrous ammonium sulphate, and again with oxalic acid. Now, it is the writer's experience with the former of these two reagents, that it sometimes happens that the salt does not contain the full amount of ferrous oxide, and the permanganate solution standardized against it, therefore, in such cases is given too high a strength. With oxalic acid the writer has never had any experience, but it is perhaps not impossible that it also is sometimes not pure, and if so, and if also Cruger and Miller had the bad luck to strike faulty samples of both these substances, then it is at once seen how their molybdenum results could come too high by the caustic soda method, and at the same time about right by their hydrogen sulphide method. The results by the caustic soda method would be too high because the strength of the permanganate used in the method was too high, and the hydrogen sulphide method results would be correct because the error

from the use of the same permanganate is counterbalanced by the loss of molybdenum in washing the sulphide. To this it will be objected that Cruger and Miller get high results by the caustic soda method even when they finish as lead molybdate, instead of titrating with permanganate. But here again an explanation is possible, which is that weighing as lead molybdate after the caustic soda separation, would also bring too high results, on account of contamination with alkali or alumina from the large amount of caustic soda used. A blank or dummy test would, of course, prevent error from alumina, if not too strongly acid with acetic acid, but not from alkali.

At any rate, it would seem to be not an unreasonable opinion that the method of Cruger and Miller is not yet placed above suspicion, and it is to be hoped that the authors will put more work on it. The writer also hopes to find opportunity to test the hydrogen sulphide separation himself, but in the meantime must disbelieve that the caustic soda method gives too high results, either by reason of a soluble iron molybdate, or for any other reason.

But the writer has found it advisable to slightly modify the manipulation as described by him in the *Iron Age*,[1] and the process now used is as follows: An 0.8 gram factor-weight is dissolved in nitric acid (also for a blank or dummy test, the same weight of some molybdenum-free steel, if the caustic soda solution is a new one), evaporated to dryness, boiled with 25 cc. strong hydrochloric acid, and evaporated to fumes with 10 cc. dilute (3:1) sulphuric acid. Taken up with 50 cc. water, and poured gradually and with shaking into 100 cc. caustic soda solution (1 pound to 2100 cc. water) contained in an 8-oz. Erlenmeyer flask provided with a file mark at 200 cc., then diluted to the mark, mixed, and 100 cc. taken of filtrate, acidified with 15 cc. strong sulphuric acid, reduced with zinc, and titrated with permanganate.

Vanadium, if present, would be reduced by the evaporation with strong hydrochloric acid, and if it then all goes into solution in the caustic soda along with the molybdenum (as seems to be the case), then the method of Glasmann[2] would seem to be the proper plan, although the writer has not yet tested it. This method determines the vanadium by reducing with zinc to the V_2O_2 form, and

[1] November 20, 1902.
[2] *Ber.*, **38**, 600.

titrating with permanganate, then in another test reducing with magnesium to the V_2O_3 form, and titrating, the difference between the two titrations showing the permanganate required to oxidize the V_2O_2 to V_2O_3. Tungsten, if present, must of course first be separated in the usual way by evaporation of the hydrochloric acid solution. But the tungsten trioxide thus obtained has a great tendency to carry down other oxides as iron, chromium and it would also seem, molybdenum; and just as the iron and chromium contamination of the tungsten trioxide must be allowed for (it is not necessary to determine this contamination in every case) so, of course, we must find and apply the correction for the molybdenum carried down with the tungsten, not for use in the tungsten determination, as there the molybdenum would volatilize in the ignition, but for use in the molybdenum test. The easiest way of determining the proportion of molybdenum carried down with various weights of tungsten trioxide, is, not to attempt a separation of the two, but to add a known amount of pure molybdenum trioxide to tungsten steels (free from molybdenum) and see how much of the molybdenum found by analysis falls short of the amount originally added; or, what amounts to the same thing, to compare results obtained in this way, using ordinary C. P. molybdenum trioxide with results obtained from the same amount of the same trioxide added to steel free from tungsten (and of course molybdenum). The following results were obtained:

No.	Tungsten. Per cent.	Molybdenum added. Per cent.	Molybdenum found. Per cent.
8661.....	17.57	8.67	8.75
8544.....	8.63	8.67	8.42
8542.....	9.64	8.67	8.58
8551.....	5.24	8.67	8.42

The greatest loss is 0.25 per cent., from which it is seen that a correction of 0.13, or half this amount, would be about the right one to employ in all cases.

In actual practice it is rare to find molybdenum and tungsten in the same steel (the writer has never had a case) for the reason that molybdenum is used as a substitute for tungsten in high speed tool steels, etc., and therefore when it is used, the tungsten is dispensed with usually.

LABORATORY OF HENRY DISSTON & SONS' STEEL WORKS.

A METHOD FOR THE DETECTION AND DETERMINATION OF ARSENIC AND ANTIMONY IN THE PRESENCE OF ORGANIC MATTER.

By F. A. Norton and A. E. Koch.

Received July 28, 1905.

The volatility of these metals precludes the incineration of organic matter containing them for their detection or estimation as is so conveniently done with most metals. A number of methods such as those of Fresenius and Babo, of Gautier, and of Danger and Flandin have been proposed, which have in view the destruction of the organic matter as completely as possible without material loss of the antimony or arsenic. All of these methods, however, fall more or less short of complete destruction of the organic matter and render subsequent determinations difficult or less satisfactory.

It occurred to us while working upon arsenic determinations in the presence of organic matter, that moist combustion with sulphuric acid might be employed to destroy the organic matter and permit of ready detection or estimation of either arsenic or antimony. This method was suggested by Pattinson's method[1] for the decomposition of arsenious sulphide with strong sulphuric acid and titration of the resulting arsenious acid with standard iodine solution for the estimation of arsenic. Sutton,[2] speaking of this method, says: "Experiments show that there is no loss of arsenious acid by volatilization when arsenious sulphide is decomposed by heating with strong sulphuric acid in the manner described." Various determinations by the authors of this paper show quite conclusively that compounds of either arsenic or antimony are not volatilized on digestion with sulphuric acid, with the exception of arsenic trichloride, and it is but slightly volatilized, if at all, when much organic matter is present. This being the case, tissues or organic matter containing arsenic or antimony, if the metal is present in sufficient quantity or if there is not too much organic matter to oxidize, may be introduced directly into a Kjeldahl digestion flask or suitable retort, and digested with concentrated sulphuric acid until clear or of a straw color. If but little arsenic or antimony is present, it would be impracticable to subject the necessary amount of the substance

[1] *J. Soc. Chem. Ind.*, **17**, 211 (1898).

[2] Sutton's "Volumetric Analysis," Ninth Edition, p. 159.

to moist combustion, and some method of extraction should be employed and the extract digested with the sulphuric acid.

For arsenic the favorite method with toxicologists where quantitative determinations are not to be made, is to digest the tissues with one-sixth hydrochloric acid for an hour at gentle boiling. A number of determinations made by us with different solvents for rapid extraction gave the best results with dilute hydrochloric acid as above. The extract obtained by straining and washing the tissues after extraction, we found could be readily digested with concentrated sulphuric acid without material loss of arsenic. Approximately 80 per cent. of the arsenic present was readily extracted by this method on each of several trials. With antimony we found that approximately 90 per cent. of the antimony as antimony and potassium tartrate could be extracted from organic matter by treatment with dilute tartaric acid instead of the hydrochloric acid, and digestion of the extract with sulphuric acid.

When it is desired to recover all of the arsenic or antimony present, the tissues, if in too large quantity to digest directly, should first be treated according to one of the more complex methods of extraction. We have found the modification of the Gautier method, as given by Peterson and Haines,[1] to give the best results for arsenic, as there is no danger of volatilization of arsenic as trichloride, hydrochloric acid not being used. With antimony, treatment of the tissues according to the method of Fresenius and Babo gives satisfactory results and is more rapid than the Gautier method.

With either metal, the first step is to obtain the arsenic or antimony free from organic matter as above with as small an excess of sulphuric acid as possible. Usually 20 cc. of sulphuric acid (sp. gr. 1.84) is sufficient to oxidize 5 grams of tissue or the extract obtained from 100 grams. If qualitative tests are to be made, the sulphuric acid residue may be diluted, and aliquot portions taken for the different tests. For the Marsh test, the addition of arsenic-free zinc in a suitable apparatus is all that is necessary, unless the acid solution has been rendered too dilute. For precipitation as sulphide or application of the Reinsch test the acid solution should be neutralized with soda and then acidified with hydrochloric acid.

[1] Peterson and Haines' "Text-book of Legal Medicine and Toxicology," Vol. II, p. 324.

QUANTITATIVE DETERMINATION.

This may be readily accomplished volumetrically by Mohr's method. The arsenic, no matter in what condition it may have been present, is reduced by the sulphur dioxide liberated in the digestion to arsenious acid, nitrates are decomposed and salts present reduced to sulphates. Thus in general no interfering bodies are left in the acid residue and after neutralization the arsenious acid can be titrated with standard iodine solution. Antimony, in the digestion with sulphuric acid, is converted into subsulphate, and on neutralization of the acid residue with potash in slight excess and acidification with tartaric acid, is converted into antimony and potassium tartrate which may be titrated with standard iodine solution, after addition of sodium bicarbonate solution.

The following determinations by the authors will show the applicability and accuracy of the method:

With Arsenic.—Four different portions of 10 grams of meat and 2.5 mg. of arsenious acid were introduced into Kjeldahl digestion flasks and digested with pure sulphuric acid until colorless or of a straw color. The flasks were then cooled, the residues diluted, nearly neutralized with soda free from oxidizable substances, and a sufficient excess of a cold saturated solution of sodium bicarbonate added, then titrated with tenth-normal iodine solution. Results follow:

	Milligrams.
Arsenious acid recovered, No. 1.....	2.47
Arsenious acid recovered, No. 2.....	2.55
Arsenious acid recovered, No. 3.....	2.45
Arsenious acid recovered, No. 4.....	2.40

In the second trial, two portions of 100 grams of finely divided meat containing 50 mg. each of arsenic trioxide were extracted by the following modification of the Gautier method as given by Peterson and Haines: To the meat in a porcelain capsule of about 600 cc. capacity were added 50 grams of strong pure nitric acid and 1 gram of pure sulphuric acid, and the mixture heated gently, at first, until liquefaction took place and the material became thick. It was then removed from the heat and 10 grams of pure sulphuric acid added, then heated again, care being taken to prevent carbonization. A little nitric acid was added from time to time until on heating it to a point where heavy vapors of sul-

phuric acid were given off, there was left in the capsule a brown liquid practically uncarbonizable at the temperature at which sulphuric acid begins to boil. When no further oxidizing effect was observed, the nitric acid was driven off by heat, the material allowed to cool, a little sulphuric acid added and the small quantity of residual brown liquid poured with constant stirring into 600 cc. of cold distilled water. The liquid was then filtered and the filtrate and washings made up to 1000 cc. Duplicate aliquot portions of the extracts representing 12.5 mg. of arsenious acid were then transferred to Kjeldahl digestion flasks, 20 cc. of sulphuric acid added, and the liquid digested until nearly clear, then neutralized and titrated as above. Results follow:

	Milligrams.
Arsenious acid recovered, No. 1.....	12.36
Arsenious acid recovered, No. 2.....	12.6
Arsenious acid recovered, No. 3.....	12.4
Arsenious acid recovered, No. 4.....	12.42

With Antimony.—Two portions of 100 grams of finely divided meat, each containing 200 mg. of pure recrystallized antimony and potassium tartrate, were treated, according to Fresenius and Babo, as follows: The meat in a porcelain capsule on a water-bath was brought to the consistency of thin gruel with distilled water, and 100 grams of pure hydrochloric acid added, then small quantities of potassium chlorate were added from time to time until the solid matters disappeared and the liquid became a clear yellow. The heat was then continued until the odor of chlorine disappeared, when the liquid was strained and the filtrate and washings made up to 250 cc. Aliquot portions of each extract representing 20 mg. of antimony and potassium tartrate were then digested with sulphuric acid, the acid residue diluted, neutralized with slight excess of potassium hydroxide, the solution slightly acidified with tartaric acid, a sufficient quantity of solution of sodium bicarbonate added and immediately titrated with tenth-normal iodine solution. Results follow:

	Milligrams.
Antimony and potassium tartrate recovered, No. 1.....	19.9
Antimony and potassium tartrate recovered, No. 2.....	19.87
Antimony and potassium tartrate recovered, No. 3.....	19.87
Antimony and potassium tartrate recovered, No. 4.....	19.95

Gravimetric methods of estimation might be desirable in some instances, though if care is taken to establish the absence of interfering substances, pure chemicals are used and the solutions are

standardized under conditions of titration, the above process would be as reliable as any volumetric determination and gives a comparatively rapid and easy method of estimation, as the moist combustion takes only from three to six hours and the titration but a few minutes. If desired, antimony or arsenic can be confirmed in the residue from the titration by either the Reinsch or Marsh tests.

Gravimetric methods may also be applied to the acid residue from the digestion of tissues or their extracts. Gravimetric results, however, obtained by us were not as satisfactory as the volumetric. Determinations of arsenic as sulphide, and antimony both as sulphide and tetroxide, after neutralization upon acid residues obtained as for the volumetric determinations, gave somewhat high results, even when the respective sulphides were dissolved with ammonia and ammonium sulphide and reprecipitated to free from contaminating salts. The estimation of arsenic as mirror, according to the method of Fresenius,[1] on the acid residue, worked very nicely, there being no frothing as in the case of employing the Gautier extract as reported by Fresenius. The results, however, were somewhat low on account of the difficulty in decomposing all of the hydrogen arsenide during its passage through the heated tube. The delicacy of this method is shown by the following experiment: A rat weighing about 200 grams was poisoned with arsenic and its liver digested with sulphuric acid until the acid residue was clear. Arsenic was then determined according to Fresenius, a distinct arsenical mirror weighing half a milligram being obtained.

SUMMARY.

Moist combustion can readily be employed to free arsenic or antimony in tissues or extracts from interfering organic matter for qualitative tests. The acid residues from the digestion of extracts or tissues can be immediately titrated, after neutralization, with standard iodine solution for the quantitative estimation of arsenic or antimony.

The acid residue from the digestion of tissues or extracts may also be employed for gravimetric determinations, or with arsenic for estimation as mirror.

CHEMICAL LABORATORY, SOUTH DAKOTA EXPERIMENT STATION.

[1] Fresenius' "Quantitative Chemical Analysis," Sixth German Edition, by Cohn, Vol. II, p. 693.

IMPROVED ORSAT APPARATUS.

By A. Bement.

Received August 12, 1905.

The instrument shown in the illustrations, was designed by the author for greater convenience of working than is possible with the regular Orsat apparatus. The distinguishing features are, that gas may be aspirated through the burette; also that absorption in the pipettes may be accomplished without displacement of the gas volume by means of the leveling bottle as is necessary with the usual pipette, so that one introduction of the gas to the pipette suffices, agitation of the reagent being accomplished by means of a simple form of pump, which consists of an orifice formed by a glass tube, to the lower end of which is attached a rubber connection, compression of which causes the reagent to be projected into the confined gas, the pipette containing no glass tubes. Babb[1] has recently described an apparatus employing a pipette wherein the gas is bubbled through the reagent. The pipette presented by the author works in an opposite manner, the reagent being sprayed or projected into the gas.

Referring to Fig. 1, gas enters by a rubber connection marked *A*, passing through a cotton filter shown, which is attached by tubing to a fitting, *B*, which takes any strain brought upon the connection. From this point the gas flows to cock *C*, which is provided with the regular three-way openings, and across the capillary connection it flows down through the burette, passes a three-way cock, *D*, at the bottom, and out by way of the connection *E*. The flow of gas through the instrument may be produced by any usual means. In this way all of the old gas is expelled and an entirely new sample is secured within the burette, after which, by manipulation of cocks *C* and *D*, it is immediately confined, and by turning cock *D* to the left-hand horizontal position, the passageway to *E* is closed and a corresponding connection established between the burette and the aspirator bottle. Then manipulation is precisely the same as with the Orsat apparatus as far as leveling and manipulation of the gas by the aspirator bottle is concerned. When the cock *D* is in position for the flow of gas by way of the passage *E*, it, of course, is closed off in the direction of the aspirator bottle. When the

[1] This Journal, **27**, 156.

sample of 100 cc. has been secured, the leveling bottle is raised and the pinch-cock at the neck of one of the pipettes is opened,

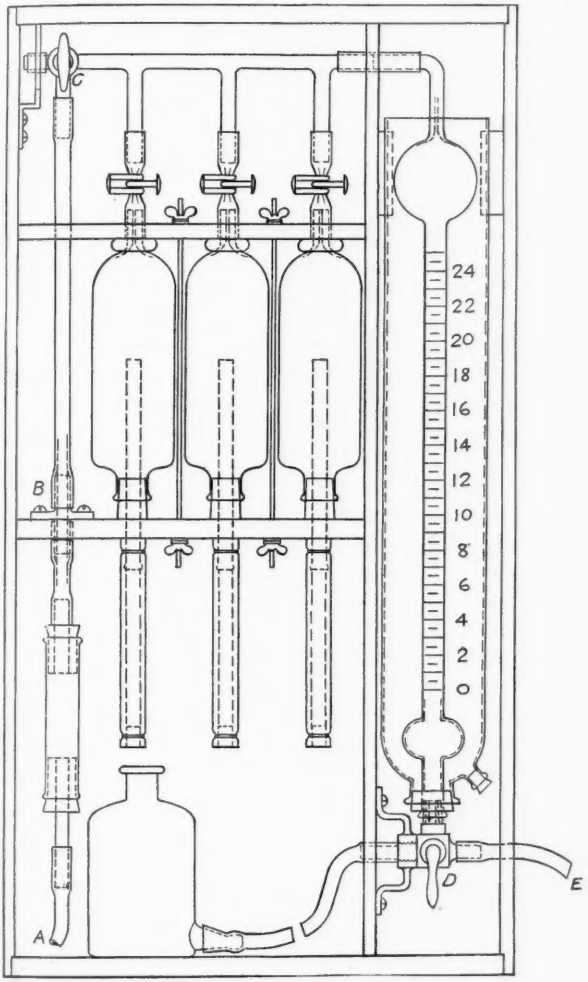


Fig. 1. Improved Orsat apparatus.

the gas being forced therein, after which the pinch-cock is closed, confining the gas to the pipette, then by compression of the

rubber projection below, the reagent is projected in jet form into the gas, which may be continued as long as necessary, after which the gas is withdrawn and measured. By this means it is often possible to secure complete absorption by one exposure in the pipette, and it is sometimes convenient when the attendant has other matters requiring his attention, to allow the gas to remain in the pipette while he gives momentary attention to other things, or the manipulation of the absorption process may continue, even if his attention is not directly upon it, which is something impossible with the usual form of pipette.

Fig. 2 is a cross-sectional elevation of the pipette and its associated features. *F* is a shelf upon which it rests, and *G* a binding-piece held down by means of rods and thumb nuts, this binding-piece being kept in place by guides located at its ends and fastened to the sides of the instrument case. *H* is a rubber washer located between the top of the pipette and the binding-piece. As will be observed, the bottom end of the pipette is closed by a pierced rubber stopper, through which a glass tube projects. The lower end of this tube has fastened upon it a piece of $^3/_8$ inch or $^7/_{16}$ inch rubber tubing closed at the lower end by a plug as indicated. The positions of the glass tubes are such that there is always a sufficient seal of the reagent over their ends. Compression of the rubber extension causes a corresponding quantity of reagent to be discharged through the tube and into the gas, and when the rubber extension is released, a similar quantity of reagent returns to its interior.

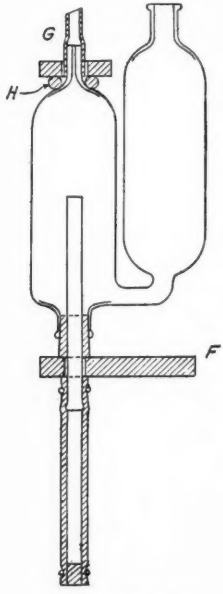


Fig. 2. Section through pipette.

The burette is surrounded by a water jacket as indicated, having at the bottom an opening provided with a stopper for drainage. The burette at its lower end has an enlargement; this is to insure that a considerable quantity of gas larger than 100 cc. is first obtained, a matter which is of considerable importance in those cases where gas may be drawn from a source at a

pressure below that of the atmosphere. In the particular instruments which the author has had made for combustion gases, the stem of the burette is of smaller diameter than usual, so that the entire contents are not greater than 28 or 30 per cent. of the burette. This makes possible finer divisions being graduated thereon, which read to 0.01 per cent.

The cock located at the lower end of the burette has in all cases been made of metal, and has proven more satisfactory than those of glass; those at the top of the pipette formerly employed, the author was compelled to replace with pinch-cocks, owing to the difficulty of obtaining carefully made and durable glass cocks.

215 DEARBORN ST., CHICAGO.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 95.]

THE USE OF THE ROTATING ANODE AND MERCURY CATHODE IN ELECTRO-ANALYSIS.

BY LILY G. KOLLOCK AND EDGAR F. SMITH.

Received August 28, 1905.

(FIRST PAPER.)

SEVERAL investigations made in this laboratory have shown that when in electro-analysis the anode is rotated, high currents can be used and metals be precipitated completely in very short periods of time; further, by the use of mercury cathodes most interesting determinations and separations of metals are possible.[1] In the latter case, however, the anode has been stationary, and the electrolyte consequently not agitated. Then, of course, the precipitation of the metal has been comparatively slow. Observing the splendid results obtained with the rotating anode, when platinum was the cathode, we determined to use a combination of rotating anode and mercury cathode. This was accordingly done, and in some preliminary trials made last August (1904), the results of which were briefly alluded to in a communication published in this Journal, **26**, 1614, mention was made that 0.4810 gram of copper could be precipitated in twenty-five minutes, and that this success could be had with other metals. Since then we have made additional experiments which we desire to record here. Not only is the time factor reduced for the metals studied, but the plan of combining a mercury cathode with the rotating anode

[1] This Journal, **25**, 884; **26**, 1124.

gives an inexpensive form of apparatus which will eliminate the platinum dish, cone or cylinder from electro-analysis and thus remove an expensive factor.

APPARATUS.

The decomposition cell is a tube 3.5 cm. in diameter and 7.5 cm. in height, made from a test-tube. Soften the bottom of the tube in a blast-lamp flame, then push through it a platinum wire 2 cm. in length, so that its end projects 0.5 cm. into the tube. Flatten the bottom of the tube on an asbestos plate and anneal it in the ordinary way.

The anode, 7.5 cm. in length, is made from platinum wire 1 mm. in diameter, coiled into a flat spiral 1.5 cm. in diameter. It is inserted in a chuck carried by the rotator which is also provided with three pulleys varying from 2 to 5 cm. in diameter. These pulleys are connected by a belt to two pulleys on the motor. With this arrangement the rotation of the anode could be varied from 100 to 1800 revolutions per minute. During the decomposition an amperemeter, a voltmeter and a rheostat, allowing of resistance from 0.1 to 100 ohms, were kept in the circuit.

The precautions indicated by Myers in his paper with regard to the decomposition cell were observed. If care be taken to have the cell as clean as possible, there will be no trouble experienced with the amalgam subsequently adhering to its sides. The mercury, before using, should be washed with alcohol and ether, and after the odor of the latter has disappeared, be placed in the desiccator until it is weighed. It was generally allowed to remain for about five minutes on the balance pan before taking the final weight. In practice a beaker containing a large quantity of mercury, so prepared, should be kept in the desiccator ready for use. The mass of the mercury taken in a single experiment varied from 40 to 50 grams. This was frequently used for two or three determinations, except in the case of chromium, where it was found advisable to use it but once. The cathode surface in the first experiments upon zinc was 3.5 sq. cm., but throughout the rest of the work it was about 9 sq. cm. After weighing the decomposition cell and mercury the solution to be electrolyzed should be introduced. The volume of the electrolyte is always recorded in the accompanying tables. The cell should then be placed upon the copper plate and the anode lowered into the solution. The distance between the

cathode and anode depended upon the volume of the electrolyte. When the volume was 5 cc. the electrodes were 0.5 cm. apart and in other instances 1 cm. was their distance apart. The difference did not appear to materially affect the rate of deposition. The tube should be covered. The anode should next be rotated and the connection made with the required number of chloride accumulator cells. The speed of the anode was varied either by using less current for the motor or by changing the combination of pulleys. With the higher currents recorded, the solution was frequently heated to boiling. When this occurred the current invariably dropped sometimes as much as 1 ampere. But upon washing down the cover-glasses with cold water, it rose to its former strength. The dropping of the current is probably due to the accumulation of steam bubbles upon the electrodes. During the electrolysis some of the solution will, of course, be carried to the sides of the containing vessel and to the cover-glasses by the escaping gases or by the agitation of the liquid. After many trials it was found that it is unnecessary to wash down this portion when the higher currents are used. The condensed steam continually frees the sides from the solution. The cover-glasses may now and then be tilted against the sides of the tube in order to run off the water which collects in large drops.

It has been repeatedly observed in the present work that the greater the concentration of the electrolyte, the greater the rapidity of deposition, but the last traces of metal were always difficult to remove. For this reason, after a solution had become colorless, the electrolytic action was continued several minutes in order to precipitate the minute amount remaining unprecipitated. It is, therefore, also important to have the volume small toward the end of the decomposition.

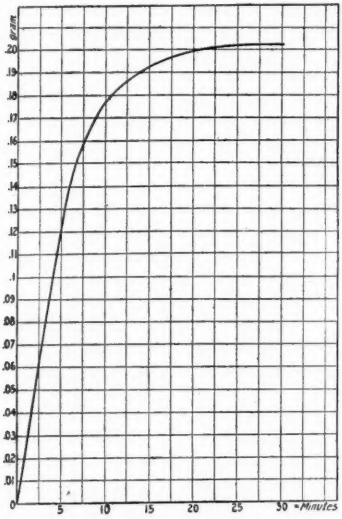
When the metal has been completely deposited, the anode should be stopped, the cover-glasses removed and the decomposition cell filled with distilled water. This should then be siphoned off to the level of the spiral and the liquid replaced by distilled water until the current drops to zero. This wash-water should always be put aside and tested in order to ascertain that the metal has been completely deposited. The current should next be interrupted and the tube removed and washed again with distilled water, inclining and twirling the cell in order to more completely wash the amalgam. As much of the water as possible should be

poured from the cell and the amalgam then be washed twice with absolute alcohol and twice with ether. It should be wiped dry on the outside and after the volatilization of the ether be placed in the desiccator and weighed as previously described.

Experimental Part.

Zinc.

The first experiments made after those described in this Journal, **26**, 1614, were upon zinc sulphate. They were conducted in order to ascertain the rate of deposition with varying concentration, current strength, electromotive force, speed of anode and how the quantity of metal in the mercury affected the subsequent rate of deposition. The solution for the first experiments contained 0.2025 gram of metallic zinc in 10 cc. This was determined by the electrolytic method, depositing it upon a plati-



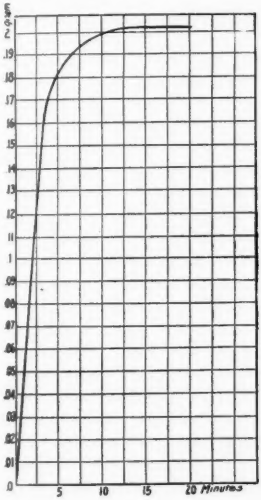
Curve 1. Zinc—1 ampere, 5 volts.

num dish from an ammonium acetate electrolyte. The speed of the anode was 400 revolutions per minute. The current strength was 1 ampere and the electromotive force was 5 volts. The volume of the zinc sulphate solution equaled 15 cc., the current acted thirty minutes. The solution siphoned from the tube

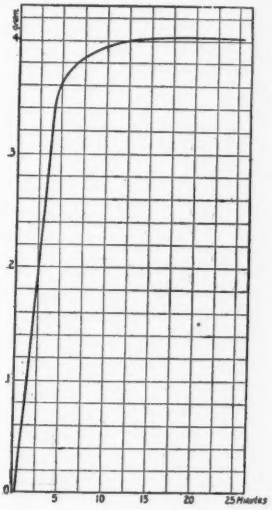
showed no trace of zinc. Consecutive experiments so conducted gave the following results in twenty-five minutes: 0.2027, 0.2030, 0.2025, 0.2025, 0.2021, 0.2027, 0.2025 gram. Two trials were made with the same conditions but using a volume of 10 cc. instead of 15 cc. It was found that the zinc was completely separated in twenty minutes.

Experiments were then made to determine the rate of deposition in successive periods of time and the curve constructed from the data thus obtained, using periods of time for abscissas and masses for ordinates. The conditions employed were those given above. The results were as follows: In five minutes, 0.1196 gram; in ten minutes, 0.1774 gram; in fifteen minutes, 0.1897 gram; in twenty minutes, 0.2002 gram; in twenty-five minutes, 0.2027 gram.

Upon employing a current of 2 amperes, adding sulphuric acid to increase the conductivity, the entire amount was deposited in



Curve 2. Zinc—2 amperes, 7 volts.



Curve 3. Zinc—2 amperes, 6 volts.

fifteen minutes. The following conditions were employed: Total volume, 15 cc.; sulphuric acid, 0.4 cc.; current strength, 2 amperes; pressure, 7 volts; speed of anode, 500 revolutions per minute.

In five minutes, 0.1860 gram of zinc was deposited; in ten minutes, 0.1998 gram; in fifteen minutes, 0.2020 gram.

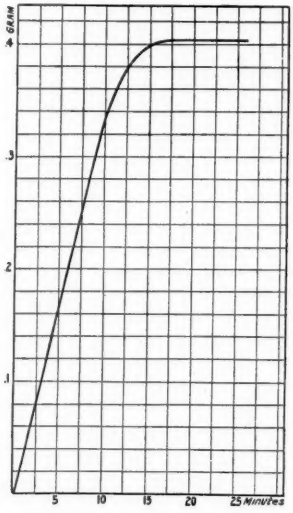
Double the quantity of zinc mentioned above was dissolved in 15 cc. To this was added 0.25 cc. of concentrated sulphuric acid, the anode was rotated at the rate of 800 revolutions per minute, and the solution electrolyzed. In thirty minutes the zinc was completely deposited, using a current of 1.5 amperes and 10 volts.

In ten minutes, 0.3701 gram was deposited; in fifteen minutes. 0.3997 gram; in twenty minutes, 0.4011 gram; in thirty minutes, 0.4058 gram.

Curve 3 was drawn from these results.

The same mass of zinc in 20 cc. was electrolyzed with a current of 2 amperes and 6 volts, other conditions being identical.

In ten minutes, 0.3352 gram was deposited; in fifteen minutes, 0.4010 gram; in twenty minutes, 0.4030 gram; in thirty minutes, 0.4050 gram.



Curve 4. Zinc—1.5 amperes, 10 volts.

Curve 4 was drawn from these results. A comparison of the third and fourth curves shows the effect of greater dilution upon the quantity of zinc deposited in the first ten minutes.

Two experiments were made to learn the effect of different

speeds of the anode upon the rate of precipitation. It was found that the amount of zinc deposited under a rotation of 440 revolutions per minute, and 1,000 revolutions per minute was only 0.0004, which is within experimental error, showing that between these limits there is no apparent effect. It was also discovered that when more than 1 gram of zinc was present in the mercury, the latter should not be further used, if it is desired to obtain results in the shortest period.

TABLE I. ZINC.

Experiment.	Zinc present. Gram.	Sulphuric acid present. cc.	Volume. cc.	Current. Amperes.	Volts.	Revolutions of anode per minute.	Time. Minutes.	Zinc found. Gram.	Error. Gram.
1	0.2025	0.0	15	1	7	750	30	0.2027	+0.0002
2	0.2025	0.0	15	1	7	750	25	0.2030	+0.0005
3	0.2025	0.0	15	1	7	750	25	0.2015	—0.001
4	0.2025	0.0	15	1	7	750	25	0.2020	—0.0005
5	0.2025	0.0	15	1	7	750	25	0.2025	....
6	0.2025	0.0	10	2	7	750	25	0.2024	—0.0001
7	0.2025	0.25	10	2	7	750	30	0.2027	+0.0002
8	0.4050	0.25	20	1.5	6	750	45	0.2054	+0.0004
9	0.2025	0.25	10	1	5	750	25	0.2025	....
10	0.2025	0.25	10	1	5	750	25	0.2029	+0.0004
11	0.2025	0.25	15	1	5	750	25	0.2025	....
12	0.2025	0.25	15	1	5	750	20	0.2027	+0.0002
13	0.2025	0.25	15	2	6	750	15	0.2030	+0.0005
14	0.2025	0.25	15	2	6	750	15	0.2020	—0 0005
15	0.2025	0.25	15	2	6	750	15	0.2021	—0.0004
16	0.4050	0.25	15	5	8	1400	6	0.4057	+0.0007
17	0.4050	0.25	15	5	8	480	6	0.4045	—0.0005
18	0.4050	0.25	15	5–6	7–5	480	8	0.4042	—0.0008
19	0.4050	0.25	10	5	7	640	5	0.4050	....

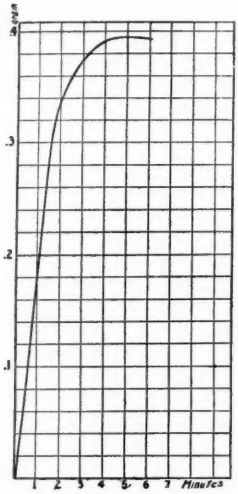
To 10 cc. of the zinc sulphate solution 0.4 cc. of concentrated sulphuric acid was added, after which it was electrolyzed by a current of 5 amperes and 7 volts, the speed of the anode being 640 revolutions per minute. Under these conditions 0.405 gram of zinc was precipitated in five minutes.

COPPER.

Having found that 0.405 gram of zinc could be deposited in from five to eight minutes it was decided to try other conditions upon copper than those recorded in the previous paper, in order

to reduce the time factor. By using higher currents and greater concentration of the electrolyte this was accomplished.

A solution of copper sulphate containing 0.3945 gram of metallic copper in 5 cc. was used for these experiments. This quantity of metal was precipitated finally in five minutes. The solution became colorless in three minutes. Twice this quantity (0.789



Curve 5. Copper—5 amperes, 6 volts.

gram) was deposited in ten minutes, although the solution had become colorless at the expiration of seven minutes. The volume in this case being 10 cc. it appeared that the last traces of copper required more time for precipitation. A current of 5 amperes and 6 volts was used, sulphuric acid being introduced to increase the conductivity.

The current strength recorded in the following table was maintained during the greater part of the electrolysis. When it showed a tendency to rise, on the liberation of the acid, additional resistance was thrown into the circuit. The following rates of deposition of copper were determined under the preceding conditions. The anode made 640 revolutions per minute. In one minute, 0.1800 gram of copper was deposited; in two minutes, 0.3400 gram; in three minutes, 0.3664 gram; in four minutes, 0.3945 gram; in five minutes, 0.3945 gram.

TABLE II. COPPER.

Experiment.	Copper present. Gram.	Sulphuric acid present. cc.	Volume. cc.	Current. Amperes.	Volts.	Revolutions of anode per minute.	Time. Minutes.	Copper found. Gram.	Error. Gram.
1	0.7890	0.25	12	3.5	6	1200	10	0.7900	+0.001
2	0.3945	0.15	12	4	6	1080	5	0.3941	—0.0004
3	0.3945	0.25	12	3.5	6	1200	6	0.3942	—0.0003
4	0.3945	0.15	12	5	6.5	1200	5	0.3944	—0.0001
5	0.3945	0.0	10	2–4	9–7	1200	6	0.3946	+0.0001
6	0.3945	0.17	10	3.5	8.5	1200	4	0.3944	—0.0001
7	0.3945	0.17	10	4	6	1080	5	0.3946	+0.0001

NICKEL.

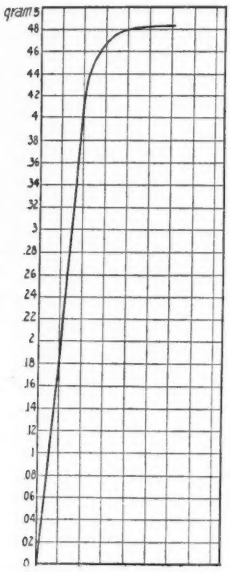
A nickel sulphate solution containing 0.4802 gram of metal in 10 cc. was used in the following experiments, and after finding that this quantity was completely deposited in the mercury in twenty minutes with a current of 2 amperes and 7 volts, the rate of deposition in succeeding periods of time was determined with a current of 2.5 amperes and 6 volts. In two and a half minutes, 0.2017 gram of nickel was deposited; in seven and a half minutes, 0.4095 gram; in ten minutes, 0.4651 gram; in twelve and a half minutes, 0.4774 gram; in fifteen minutes, 0.4802 gram.

TABLE III. NICKEL.

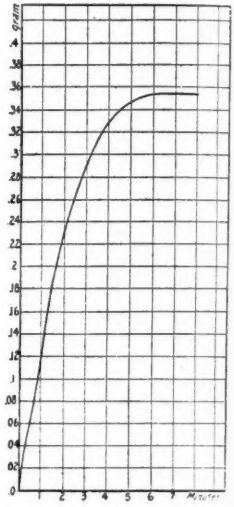
Experiment.	Nickel present. Gram.	Sulphuric acid. cc.	Volume. cc.	Current. Amperes.	Volts.	Revolutions of anode per minute.	Time. Minutes.	Nickel found. Gram.	Error. Gram.
1	0.4802	0.25	18	2	7	600	18	0.4802	....
2	0.4802	0.25	12	3.5	7	600	16	0.4799	—0.0003
3	0.4802	0.25	12	2–4	6.5	600	10	0.4806	+0.0004
4	0.4802	0.25	12	6	5	500	7	0.4804	+0.0002
5	0.4802	0.25	12	5	6.5	600	10	0.4796	—0.0006
6	0.9604	0.25	10–30	4	6	1100	10	0.9597	—0.0007
7	0.4802	0.25	12	3	7–5	1100	10	0.4806	+0.0004
8	0.4802	0.25	12	3	7	1100	10	0.4796	—0.0006
9	0.9604	0.25	12	3.5	7	1100	16	0.9604	....
10	0.4802	0.25	12	5	7	640	12	0.4809	+0.0007
11	0.4802	0.25	12	5	6	880	8	0.4806	+0.0004
12	0.4802	0.25	7	6	5	1200	9	0.4801	—0.0001
13	0.4802	0.25	7	6	6	1200	7	0.4801	—0.0001

On employing a current of 6 amperes and a pressure of 5 volts, the solution became colorless in four minutes. Not a trace of

nickel was found in the liquid after seven minutes. The amalgam was very bright and of the consistency of soft dough, when 1 gram of nickel was combined with the usual quantity of mercury (40 grams).



Curve 6. Nickel—2.5 amperes, 6 volts.



Curve 7. Cobalt—5 amperes, 5 volts.

COBALT.

This metal does not appear to enter the mercury with the same rapidity as nickel under similar conditions. The last minute traces are more difficult to remove. Various conditions were used. When no sulphuric acid was added the current was at first low, but it rapidly rose as the decomposition proceeded. The conditions, giving the total cobalt in the least time, were the following: 10 cc. of solution, containing 0.3535 gram of cobalt; 0.25 cc. of sulphuric acid and a current of 5 amperes with a pressure of 6 volts. The speed of the anode was 1,200 revolutions per minute. The solution became colorless in seven minutes, but ten minutes appeared to be necessary for the removal of the last traces of the metal. On using the same amount of cobalt in a volume of 5 cc., other conditions remaining unchanged, all of the metal sep-

arated in seven minutes, thus: In one minute, 0.1197 gram of cobalt was deposited; in three minutes, 0.2930 gram; in five minutes, 0.3300 gram; in six minutes, 0.3520 gram; in seven minutes, 0.3535 gram; in ten minutes, 0.3530 gram.

The curve (7) was constructed from these results.

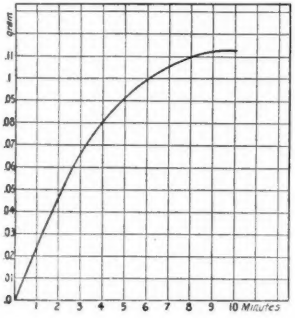
TABLE IV.—COBALT.

Experiment.	Cobalt present. Gram.	Sulphuric acid present. cc.	Volume. cc.	Current. Amperes.	Volts.	Revolutions of anode per minute.	Time. Minutes.	Cobalt found. Gram.	Error. Gram.
1	0.3525	0.35	15	5	7	1250	15	0.3522	—0.0003
2	0.3525	0.25	15	3	5	980	18	0.3524	—0.0001
3	0.3525	0.25	15	4	6	600	14	0.3523	—0.0002
4	0.3525	0.25	10	4	6	860	16	0.3530	+0.0005
5	0.3525	0.5	10	4	6	1000	15	0.3530	+0.0005
6	0.3525	0	10	4	6	1240	16	0.3528	+0.0003
7	0.3525	0.25	10	3	6	1200	10	0.3521	—0.0004
8	0.3525	0.5	10	6	6	1200	10	0.3530	+0.0005
9	0.3525	0.25	10	5	8	800	10	0.3522	—0.0003
10	0.3525	0.25	10	3	8	1400	12	0.3523	—0.0002
11	0.3525	0.5	10	6	5	800	11	0.3530	+0.0005
12	0.7050	0.5	15	6	7	1200	30	0.7052	+0.0002
13	0.1762	0.35	10	4	8	560	7	0.1762	....

CHROMIUM.

A solution of chromium sulphate was electrolyzed with currents varying from 1 to 4 amperes and 7 to 12 volts, and with a varying quantity of sulphuric acid. It was found by Myers that the addition of the acid was necessary, otherwise, there was a separation of the oxide of chromium throughout the liquid; but too much acid retards or entirely prevents the decomposition. When 10 drops (40 drops = 1 cc.) were added and a current of 2.5 amperes and 6 volts applied, one half hour was necessary to deposit 0.23 gram of chromium. With 0.5 cc. of acid and a current of 5 amperes and 4 volts, the solution at the end of sixty minutes did not appear to have lost its color. Experiments were then made to learn how much chromium, if any, was deposited when the acid was present in large quantity. Thus, with a current of 4 amperes and 7 volts, the solution containing 1 cc. of acid, 0.05 gram of metal was precipitated in forty-five minutes, while with 2 cc. of acid and a current of 1 ampere and 4 volts the mercury showed no increase in weight after thirty minutes. The following results, ob-

tained with the use of smaller amounts of acid, confirm this. By adding 10 drops of acid (=0.25 cc.) and employing a current of 4 amperes and 7 volts, the liquid became colorless in thirty minutes, but forty minutes were necessary for the complete removal of the metal. With the same quantity of acid, and a current of 5 amperes and 8 volts, the chromium was completely precipitated in thirty minutes. With five drops of acid and a current of 3 to 4.5 amperes and 8 volts, the solution became colorless in eleven minutes. It, therefore, seems that more than three drops of acid are sufficient to materially affect the rate of precipitation. More than two drops of acid must be present to prevent the separation of chromic oxide



Curve 8. Chromium—3.5 amperes, 11-10 volts.

which always took place with less than that amount of acid. The following conditions gave the most rapid determination: A volume of the solution, containing 0.1190 gram of chromium and three drops of sulphuric acid (40 drops = 1 cc.), was electrolyzed with a current of 4 to 5 amperes and 6 volts, the speed of the anode being 400 revolutions per minute. In four minutes the solution was colorless and in six minutes the chromium was found to be completely deposited. The solution was siphoned off in the manner previously described, but after the cell was removed anhydrous alcohol was poured in as quickly as possible and the operation repeated twice and followed by two washings with ether in order to prevent, if possible, oxidation of the chromium. Oxidation, if it occurred, was but slight, for the error never exceeded 0.0007 gram.

Curve 8 was constructed from the results given below: In two minutes, 0.048 gram of chromium was deposited; in four minutes,

0.085 gram; in six minutes, 0.1000 gram; in eight minutes, 0.1105 gram; in nine minutes, 0.1185 gram; in ten minutes, 0.1185 gram.

TABLE V.—CHROMIUM.

Experiment.	Chromium present. Gram.	Sulphuric acid (40 drops = 1 cc.).	Volume. cc.	Current. Amperes.	Volts.	Revolutions of anode per minute.	Time. Minutes.	Chromium found. Gram.	Error. Gram.
1	0.1180	5	10–15	3–4	7	280	15	0.1186	+0.0006
2	0.1180	3	10–15	2–4	11–9	280	15	0.1187	+0.0007
3	0.1180	3	10–15	1–3	9	640	20	0.1185	+0.0005
4	0.1180	3	8–15	1.5–3	10–8	220	15	0.1186	+0.0006
5	0.1180	3	10–15	1–3	11–9	520	20	0.1186	+0.0006
6	0.1180	3	5–15	1–2	11–9	640	17	0.1175	—0.0005
7	0.1180	3	5–15	2–4	9–8	480	15	0.1180	....
8	0.2360	3	5–15	2.5	10	520	50	0.2355	—0.0005
9	0.1180	5	5–15	3	7.5	400	15	0.1179	—0.0001
10	0.1180	3	7–15	4–5	8	640	6	0.1175	—0.0005
11	0.1180	3	7–15	3–4	10–9	640	10	0.1180	....
12	0.1180	7	7–15	3–4	10–8	200	13	0.1187	+0.0007
13	0.1180	3	5–15	3.5	8	640	11	0.1177	—0.0003
14	0.2360	4	5–15	3	12	640	35	0.2359	—0.0001
15	0.1180	3	5–15	3–4	10–8	320	11	0.1179	—0.0001
16	0.1180	3	5–15	3–4	10	540	11	0.1182	+0.0002

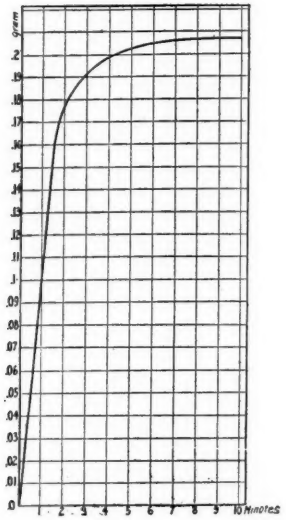
IRON.

In experimenting with salts of this metal it was soon discovered that sulphuric acid in large amount retarded its precipitation. It was also noticed when higher currents were used that the solution became very hot and assumed a decidedly pink color,[1] which disappeared on the addition of cold water or when the cover-glasses were removed, allowing the steam to escape rapidly and thus decreasing the pressure and consequently the temperature of the boiling solution. The color reappeared a few seconds after the cover-glasses were replaced.

The conditions which gave the most satisfactory results were as follows: Volume of solution 5 cc. containing 0.275 gram of metallic iron, 3 drops of concentrated sulphuric acid and a current of 3 to 4 amperes and 7 volts. The rotation of the anode varied from 520–920 revolutions per minute. The iron was completely deposited in seven minutes. The following observations on rate of deposition were made under the conditions just given: In two minutes, 0.1760 gram of iron was deposited; in four minutes,

[1] Due to traces of manganese.

0.2000 gram; in six minutes, 0.2050 gram; in eight minutes, 0.2075 gram.



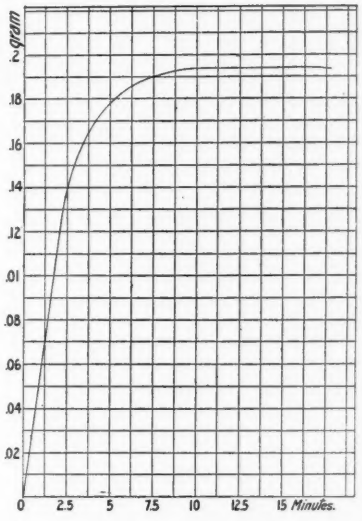
Curve 9. Iron—3.5 amperes, 7 volts.

In addition to the results just described a solution of ferrous sulphate containing 0.1945 gram of iron in 10 cc. was used to get further working conditions. By using a current of 3.5 amperes and 10–9 volts, with about 900 revolutions per minute of the anode, the total iron content was deposited in fifteen minutes. The

TABLE VI.—IRON.

Experiment.	Iron present. Gram.	Sulphuric acid in drops (40 drops=1 cc.).	Volume. cc.	Current. Amperes.	Volts.	Revolutions of anode per minute.	Time. Minutes.	Iron found. Gram.	Error. Gram.
1	0.2075	7	5	4–5	8–7	520	14	0.2072	—0.0003
2	0.2075	4	5–15	5–4	6.5–5	680	14	0.2078	+0.0003
3	0.2075	5	5–10	3.2–4	6.5	680	15	0.2077	—0.0003
4	0.2075	3	5	2–2.5	7–6	680	15	0.2073	—0.0002
5	0.2075	3	5	4	6–5	680	10	0.2080	+0.0005
6	0.2075	3	5	3–4.5	7–6	920	7	0.2078	+0.0003
7	0.2075	3	5	2–3	6	740	9	0.2076	+0.0001
8	0.2075	3	5	2–4	6.5–5.5	700	9	0.2076	+0.0001

residue from the decomposition cell, when oxidized by nitric acid and tested with potassium sulphocyanide, gave no color. The experiments made to determine the rate of deposition with a lower current (1–2.5 amperes and 10–9 volts), while the other conditions



Curve 10. Iron—1 to 2.5 amperes, 10-9 volts.

remained as above, gave the following results which appear in Curve 10.

In two and a half minutes, 0.1141 gram of iron was deposited; in five minutes, 0.1787 gram; in seven and a half minutes, 0.1945 gram; in ten minutes, 0.1950 gram.

When the residue was tested with potassium sulphocyanide no iron was detected. By the addition of 3 drops (40 drops = 1 cc.) of sulphuric acid and using a higher current (3.5 amperes) in ten minutes a faint reaction for iron was observed, indicating that the acid has some retarding influence. In fifteen minutes under these conditions the iron had completely separated. By using a higher current, 3 amperes and 9 volts, under the same condition, all the iron was deposited in ten minutes.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 93.]

THE ELECTROLYTIC DETERMINATION OF MERCURY WITH THE USE OF A ROTATING ANODE.[1]

BY RALPH O. SMITH.

Received August 28, 1905.

ONE OF the very first electrolytes applied in the electrolytic determination of mercury was a solution of the nitrate or chloride of the metal acidulated with nitric acid. The time required for the deposition of the metal varied from twelve to sixteen hours, but by heating the electrolyte to 70° four hours were sufficient for the complete precipitation.

Exner,[2] by the use of a rotating anode and a high current density, was able to precipitate 0.5 gram of mercury in twelve minutes. He used a solution of mercurous nitrate acidulated with 1 cc. of concentrated nitric acid.

Fischer and Boddaert[3] were able to confirm Exner's work, but used a little longer period—about twenty minutes—for the precipitation.

The following experiments were made to determine the rate at which, with the help of a rotating anode, it was possible to precipitate mercury from a solution of mercurous nitrate. The electrolyte consisted of 25 cc. of mercurous nitrate solution (equal to 0.2560 gram of mercury) and 1 cc. of concentrated nitric acid (sp. gr. 1.17), with a total dilution of 115 cc.

TABLE I.

Experiment.	Time. Minutes.	Mercury found.	Volts.	N.D.$_{100}$ amperes.
1	2	0.2040	6.5	7.4–7
2	4	0.2387	7.7–7.5	7.6–8
3	6	0.2477	7.9–8	7 –7.1
4	8	0.2559	7	7.2–6.9
5	10	0.2558	7 –7.4	7 –7.1
6	15	0.2561	7 –6.7	7.3–6.9
7	20	0.2558	7	7.4–7
8	20	0.2561	8.4–6.2	7.2

The residual liquid from Expts. 4, 5, 6, 7, and 8 gave no test for mercury. In experiment 8 the electrolyte was not previously

[1] From the author's thesis for the Ph.D. degree.

[2] This Journal, **25**, 896.

[3] *Z. Elektrochem.*, **10**, 950.

heated; the others had been heated. No difference was noted, hence there was evidently no loss of mercury in the other experiments.

To further confirm the preceding observations 50 cc. of mercurous nitrate solution, containing 1 cc. of concentrated nitric acid (sp. gr 1.17), were diluted to 115 cc. and electrolyzed. These conditions were repeated in each of the following experiments:

TABLE II.

Experiment.	Time. Minutes.	Mercury found.	Volts.	N.D 100 amperes.
9	2	0.3612	6 –7	7.1–7.2
10	4	0.4772	6.3–6.6	7.2
11	8	0.5077	6.7–6.6	7.3–7.1
12	10	0.5122	6.4–6.3	7.2–7.1
13	12	0.5121	7 –6.6	7.2–7
14	20	0.5119	6 –6.4	7.2–7

From the preceding results the time curves, as shown in Fig. 1, were drawn.

In speaking of this method of precipitating mercury Exner mentions that the dish used as a cathode lost 0.0006 gram in weight in three experiments. In the present study a greater loss in the weight of the platinum cathode was noted. A dark film of platinum black always remained when the mercury deposit was dissolved from off the dish with hot nitric acid. It was removed by polishing with sand. The loss in weight of the dish was on an average 1.5 mg.

The time required for the precipitation of 0.25 gram of mercury from this electrolyte was eight minutes, while ten minutes proved sufficient for the precipitation of 0.5 gram of the metal.

Another electrolyte which was found most satisfactory in the electrolytic determination of mercury was that of an alkaline sulphide.[1] It also proved to be most helpful because it could be applied directly to ores of mercury, for example, cinnabar. It remained, however, to determine the rate at which mercury might be completely precipitated from this electrolyte, using a rotating anode. Accordingly, a solution of mercuric chloride was prepared, 25 cc. of which contained 0.2603 gram of mercury. This is the quantity which was used in the experiments given below.

[1] Smith's "Electrochemical Analysis," p. 74 (1902).

TABLE III.

Experiment.	Time. Minutes.	Mercury found.	Sodium sulphide (sp. gr. 1.17). cc.	Volts.	N.D 100 amperes.
1	10	0.1959	..	10.5–10	5 –6.3
2	10	0.2582	10	7 –6.8	6 –6.2
3	10	0.2576	10	10 –7.7	10.1–9.6
4	10	0.2554	20	5.3–5.7	6 –5.8
5	12	0.2596	10	7.5–7	6 –6.2
6	13	0.2601	10	6.7–6.6	6
7	15	0.2602	10	7 –6.6	6 –5.9
8	15	0.2571	10	9.3–7.1	6 –6.2
9	20	0.2604	10	7 –6.5	6
10	25	0.2605	10	6.9–6.4	6 –5.9
11	8	0.2538	10	6.8–6.7	6 –6.2
12	5	0.2198	10	7	6.1–6.2
13	2	0.1371	10	6 –6.6	6 –6.2

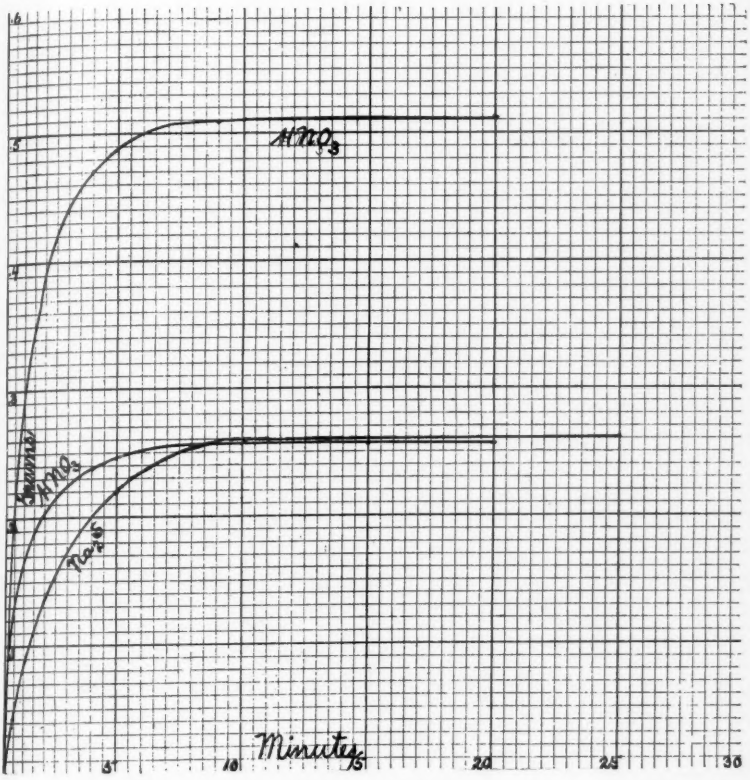
In Expt. 1 mercury sulphide had separated upon the surface and the sides of the liquid before electrolysis took place. As this material did not dissolve, the result is naturally low. The separation may be prevented by adding a sodium sulphide solution to that of the mercury salt before dilution.

In Expt. 3 the effect of a higher current density was tried without any apparent advantage. No beneficial result was observed in Expt. 4 by the use of a larger amount of sodium sulphide.

The residual liquid from Expts. 2, 3, 4, 5 and 8, when digested with an ammonium nitrate solution, showed the presence of mercury, but it could not be detected in the liquid from Expts. 6, 7, 9 and 10. The fact that more time was required for the precipitation of the mercury in Expt. 8 is due to the use of a cold electrolyte.

Expts. 11, 12 and 13 were conducted to learn how much metal was precipitated in two, five and eight minutes respectively, so that the data for the time curve, page 1273, might be complete.

In performing these experiments the alkaline liquid was in each instance siphoned off without interrupting the current, fresh water being added as it was removed until the ammeter stood at zero. The current was then interrupted and the deposit of metal washed with absolute alcohol and ether, the dish being warmed between the hands to remove the last traces of ether. After wiping the outside of the dish with a clean, soft cloth, it was allowed to stand in a desiccator for twenty minutes before weighing. It was found that the precipitated metal weighed the same



Rate of deposition of mercury.

after standing twenty minutes as after standing twenty-four hours.

The deposit of mercury was dissolved from off the dish with hot nitric acid (1:1). The insoluble film of platinum black invariably remained upon the dish, indicating that the mercury had penetrated the platinum and formed an amalgam with it. In each experiment the dish lost in weight about 0.0025 gram.

The preceding results show that this electrolyte answers admirably for the rapid determination of mercury.

A sample of California cinnabar was distilled with lime, and

showed the presence of 46.26 per cent. of mercury. Weighed portions of this same ore were heated to boiling with 20 cc. of sodium sulphide (sp. gr. 1.06) in a small beaker. The insoluble portion was allowed to subside and the supernatant liquid poured through a filter into a weighed platinum dish. The gangue was treated with a second portion of 10 cc. of sodium sulphide, and the solution filtered as before. This operation was repeated a third time and the gangue finally washed with hot water by decantation, and then thrown upon the filter, where it was washed until the filtrate was neutral to litmus.

The solutions obtained in this way were electrolyzed. A little longer period was required for the precipitation, as will be observed below, because the electrolyte was not heated at the beginning. The results follows:

TABLE IV.

Experiment.	Time. Minutes.	Sodium sulphide (sp. gr. 1.06). cc.	Ore.	Mercury found.	Per cent.	Volts.	$N.D_{100}$ amperes.
1	15	40	0.3007	0.1380	45.88	6.2–6.1	6 –6.2
2	20	40	0.3002	0.1393	46.40	6.3–5.7	6
3	25	40	0.3002	0.1395	46.46	6.9–5.7	6 –6.2
4	30	40	0.3004	0.1394	46.40	6.6–5.5	6.2–6.4
5	20	60	0.5003	0.2322	46.41	6 –5.1	6
6	25	60	0.5002	0.2321	46.40	5.6–4.9	6.2–6
7	30	60	0.5003	0.2325	46.46	5.8–5	6 –6.2

They show conclusively that the precipitation may be made in twenty minutes, no mercury having been detected in the residual liquid.

The time necessary for each of the above analyses did not exceed an hour and thirty minutes from the weighing out of the ore until the weight of the deposit had been obtained.

The gangue in each experiment was dried and ignited with lime. No mercury was found. In those cases where one-half gram of ore was used the quantity of sodium sulphide applied to its solution amounted to 60 cc.

It goes without saying, after an inspection of the above results, that the electrolytic procedure for the determination of mercury in its ordinary salts and in its most common and important ore is vastly superior to the time-honored method of distillation with lime, and indeed to any other method which has been applied for its estimation.

The deposits of mercury were always adherent and very satisfactory, so that we feel that this course may be recommended without hesitation to analysts.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 92.]

THE ELECTROLYTIC DETERMINATION OF CADMIUM WITH THE USE OF A ROTATING ANODE.[1]

BY ALICE L. DAVISON.

Received August 28, 1905.

INTRODUCTION.

IN VIEW of the work recently done in the rapid determination of metals electrolytically by the use of a rotating anode[2] it has seemed desirable to investigate each metal separately, studying the conditions under which it may be precipitated from different electrolytes. In this way, zinc, nickel and cobalt have been studied,[3] and data accumulated relating to the rapid precipitation of these metals. The purpose of the present work was to make a similar study of cadmium.

This metal may be determined easily and accurately by the electric current from a number of electrolytes, and its deposition by the aid of a rotating anode was shown by Exner[3] to be accomplished completely in a very short time. The apparatus used in the present investigation was the same as that employed by Exner, Ingham and Ashbrook[3] working in this laboratory, and the same general method of procedure was followed. The dilution of the electrolyte was from 90–125 cc., giving an average cathode surface of 100 sq. cm., and the average distance between the electrodes was 1 cm. With the motor used, six speeds of rotation were practicable for the anode, *viz.*, 430, 580, 630, 700, 810 and 840 revolutions, respectively, per minute. These are designated in the tabulated conditions by the numerals I to VI.

In each electrolyte special attention was given to the determination of the rate of precipitation, and the results were plotted graphically. In every case the solution, before electrolyzing, was heated until bubbles appeared on the bottom of the dish.

[1] From author's thesis for the Ph.D. degree.

[2] This Journal, **25**, 896; **26**, 1251, 1269, 1283, 1595.

[3] *Loc. cit.*

Experimental Part.

(A) Sulphuric acid electrolyte.

Wrightson[1] maintained that results obtained in the use of cadmium sulphate solutions were far from satisfactory, but it was later demonstrated[2] that he was in error. The conditions used by Exner in depositing cadmium from this electrolyte were useful as a guide in the further study of it. It was found that a large quantity of acid retarded the complete deposition of metal, and that the small amounts used in the experiments here recorded seemed favorable to the best results. The rate of deposition from this electrolyte is shown, together with that from the other inorganic electrolytes, in Fig. 1. The deposits were gray, crystalline, and quite adherent.

Table I.

$CdSO_4$ =⊃= Cd. Gram.	H_2SO_4. 1 : 10 cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.2867	1.0	3–5	13	III	15	0.2866
0.2867	1.0	5	13	III	14	0.2869
0.2867	0.5	3	13	III	1	0.1020
0.2867	0.5	3	13	III	2	0.1669
0.2867	0.5	3	13	III	5	0.2857
0.2867	0.5	3	12	III	7½	0.2860
0.2867	0.5	3	12	III	8	0.2861
0.2867	0.5	3	12	III	9	0.2867
0.2867	0.5	3	12	III	15	0.2867
0.5760	0.5	4	14	III	1	0.1190
0.5760	0.5	4	14	III	2	0.2245
0.5760	0.5	4	14	III	3	0.3417
0.5760	0.5	4	14	III	5	0.5217
0.5760	0.5	4	14	III	7½	0.5760
0.5760	0.5	4	14	III	8	0.5762

It was thought by adding a few cubic centimeters of ammonium hydroxide when most of the metal had been precipitated, that the last traces of cadmium would be brought down more quickly. This was shown to be true by the following results:

Table II.

$CdSO_4$ =⊃= Cd. Gram.	H_2SO_4. 1 : 10 cc.	NH_4OH. cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.2867	0.5	2	3	13	III	5 } 2 }	0.2868
0.2867	0.5	2	3	13	III	5 } 1 }	0.2870
0.2867	0.5	2	3	13	III	5 } 1 }	0.2870

[1] *Z. anal. Chem.*, **15**, 303.

[2] *Am. Chem. J.*, **2**, 42.

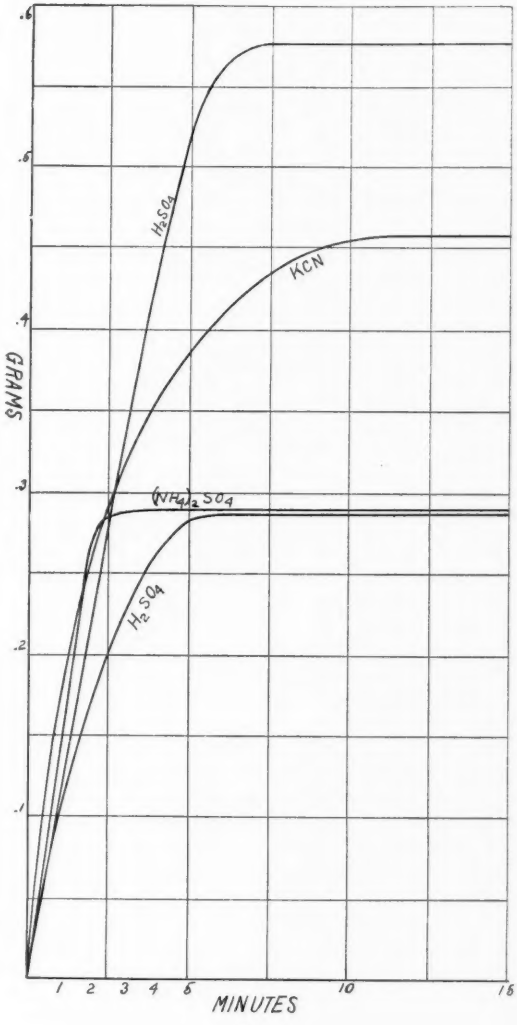


Fig. 1.

(B) AMMONIUM HYDROXIDE AND AMMONIUM SULPHATE ELECTROLYTE.

Clarke[1] attempted the precipitation of this metal from an ammoniacal solution. It was deposited in such a spongy non-adherent form that analysts since his day have wholly discarded solutions containing such salts. Since, however, Ingham[2] proved that zinc was deposited quantitatively and satisfactorily from an ammoniacal solution by the aid of a rotating anode it was thought that cadmium also might be determined in this way. Cadmium hydroxide was precipitated and redissolved by ammonium hydroxide, and then sulphuric acid neutralized by ammonium hydroxide was added to increase the conductivity. With a current of 5 amperes gray deposits were obtained, which, though somewhat spongy, were quite adherent and satisfactory. The liquid was always alkaline at the end of precipitation.

TABLE III.

$CdSO_4$ =○= Cd. Gram.	NH_4OH. cc.	H_2SO_4. 1 : 10 cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.2887	5+6	10	5	6½	II	10	0.2887
0.2887	5+6	10	5	6	II	10	0.2886
0.2887	5+6	10	5	6½	II	10	0.2885
0.2887	5+6	10	5	6	II	10	0.2888
0.2887	5+6	10	5	6	II	1	0.1312
0.2887	5+6	10	5	6	II	2	0.2708
0.2887	5+6	10	5	6	II	3	0.2868
0.2887	5+6	10	5	6	II	5	0.2889
0.2887	5+6	10	5	6	II	6	0.2887
0.2887	5+6	10	4 6 7	5 6½ 6¾	II	3 1 1	0.2879
0.2887	5+6	10	4 6 8	5 6½ 7½	II	2 2 1	....
0.2887	7+6	10	5 6	5 6½	II	4 1	0.2879
0.2887	5+12	10	5 6	6½ 6½	II	4 1	....

An attempt to shorten the time of deposition by increasing the current and the amount of ammonium hydroxide is shown by

[1] *Z. anal. Chem.*, **18**, 104.

[2] *Loc. cit.*

the last four experiments to have been unsuccessful, the only result being to increase the sponginess of the deposit, in two instances to such a degree that weighing was omitted. The rate of precipitation from this electrolyte is represented graphically in Fig. 1.

(C) SODIUM FORMATE ELECTROLYTE.

Formic acid as an electrolyte for the determination of cadmium was first suggested by Warwick[1] and later used by Avery and Dales.[2] Ingham also demonstrated that with a rotating anode formic acid was an excellent electrolyte for the deposition of zinc, and the conditions recommended by him were used as a guide in the following experiments with cadmium. From this electrolyte the metal was completely precipitated in four minutes as a dark gray, spongy, though adherent deposit, the liquid siphoned off giving no test for cadmium. The following results prove that the quantity of sodium formate may vary widely.

TABLE IV.

$CdSO_4$ =⊃= Cd. Gram.	Na_2CO_3. Grams.	HCOOH (sp. gr. 1.06). cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.2898	5	16	5	5	II	15	0.2900
0.2898	4	15	5	5½	II	15	0.2903
0.2898	3	10	5	6½	II	15	0.2902
0.2898	2	8	5	7	II	10	0.2898
0.2898	1	4	5	11½	II	10	0.2894
0.2898	1.2	5	5	8	II	1	0.1645
0.2898	1.2	5	5	8	II	2	0.2816
0.2898	1.2	5	5	9	II	3	0.2891
0.2898	1.2	5	5	8½	II	4	0.2896

(D) AMMONIUM FORMATE ELECTROLYTE.

After the satisfactory results obtained from the use of sodium formate as an electrolyte, ammonium formate was suggested. Ammonium hydroxide was added in excess, and then varying amounts of formic acid. The results indicate that the liquid may be either alkaline or acid without affecting the deposit or the time.

[1] *Z. anorg. Chem.*, **1**, 258.

[2] This Journal, **19**, 380.

TABLE V.

$CdSO_4$ =○= Cd. Gram.	NH_4OH. cc.	HCOOH (sp. gr. 1.06) cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.2898	5	5	5	6	II	5	0.2900
0.2898	5	10	5	6	II	5	0.2910
0.2898	5	10	5	5	II	5	0.2898
0.2898	5	6	5	6	II	5	0.2899
0.2898	5	6	5	5½	II	1	0.1612
0.2898	5	6	5	6	II	2	0.2850
0.2898	5	6	5	6	II	3	0.2904
0.2898	5	10	5	5	II	1	0.1766
0.2898	5	10	5	6	II	2	0.2870
0.2898	5	10	5	6	II	3	0.2904

The deposits from this electrolyte were very similar to those from a sodium formate solution, and the time curves of the two electrolytes nearly coincide, as is seen in Fig. 2.

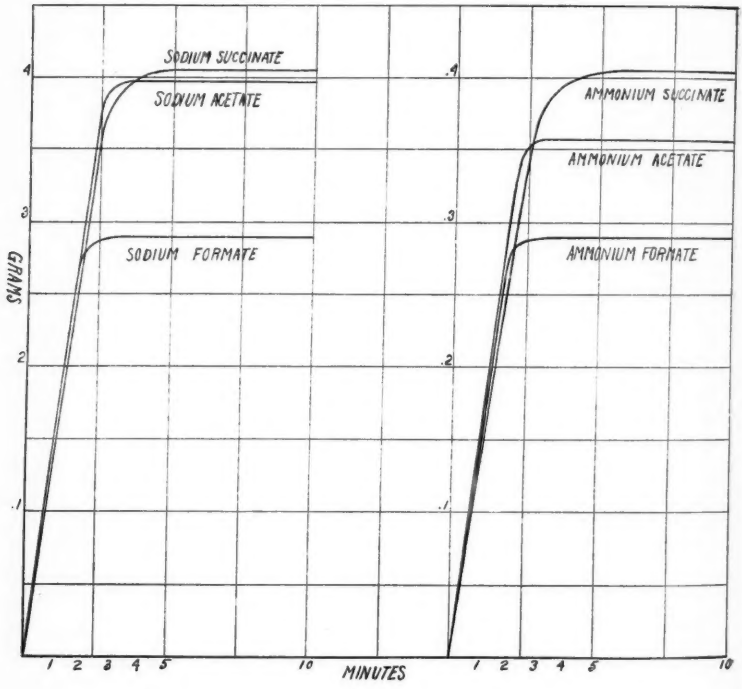


Fig. 2.

(E) SODIUM ACETATE ELECTROLYTE.

This electrolyte was one of the first from which cadmium was successfully precipitated,[1] and has usually been conceded to be one of the most satisfactory means of obtaining the metal electrolytically.[2] With the rotating anode Exner got excellent results from this electrolyte, but his conditions were not used, more sodium acetate being added, and a small amount of acetic acid being substituted for the potassium sulphate which was added to increase the conductivity. The electrolyte proved to be very like the formate solutions in its resulting deposits. The rate of precipitation from both sodium acetate and ammonium acetate will be seen to be very rapid (Fig. 2).

TABLE VI

$CdSO_4$ => Cd. Gram.	$NaC_2H_3O_2$. Grams.	$HC_2H_3O_2$. cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.1992	3	0.25	5	8½	II	10	0.1992
0.1992	3	0.25	5	8½	II	10	0.1992
0.3984	3	0.25	5	8½	II	1	0.1601
0.3984	3	0.25	5	8½	II	2	0.2863
0.3984	3	0.25	5	8½	II	3	0.3963
0.3984	3	0.25	5	9	II	4	0.3987

(F) AMMONIUM ACETATE ELECTROLYTE.

That an alkaline acetate electrolyte is inferior to one that is acid was shown by the following experiments. At the beginning a slightly acid solution of ammonium acetate was used. The results of sixteen experiments were as follows:

TABLE VII.

$CdSO_4$ => Cd. Gram.	$NH_4C_2H_3O_2$. Grams.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.4000	3	5	7	II	10	0.4010
0.4000	2	5	9½	II	10	0.3997
0.4000	2	5	8½	II	10	0.4002
0.4000	2	5	8½	II	10	0.3993
0.4000	2	5	8½	II	10	0.3989
0.4000	2	5	8½	II	1	0.1617
0.4000	2	5	9	II	2	0.3255
0.4000	2	5	8½	II	3	0.3928
0.4000	2	5	9	II	4	0.3981
0.4000	2	5	9	II	5	0.3990
0.4000	2	5	9	II	6	0.3995
0.4000	2	5	9½	II	7	0.3995
0.4000	2	5	9½	II	8	0.3994
0.4000	2	5	9½	II	9	0.4002
0.3588	2	5	8½	II	10	0.3588
0.3588	2	5	9½	II	10	0.3588

[1] *Am. Phil. Soc. Proc.*, 1878; *Z. anal. Chem.*, **19**, 16.

[2] This Journal, **19**, 870: *C. R.*, **131**, 384.

It was evident from these experiments that the last traces of metal were very hard to precipitate, so that a series of four trials was made in which a few cubic centimeters of ammonium hydroxide were added after the electrolysis had proceeded three minutes. The result was to hinder deposition. Then the addition of 3 cc. of acetic acid after two minutes was tried, with the following satisfactory results. In the last five experiments the excess of acid was present from the beginning. The deposits were excellent.

TABLE VIII.

$\frac{CdSO_4}{4}$ = Cd. Gram.	$NH_4C_2H_3O_2$. Grams.	$HC_2H_3O_2$. cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.3575	2	3	5	$8\frac{1}{2}$	II	5	0.3575
0.3575	2	3	5	8	II	5	0.3574
0.3575	3	3	5	$8\frac{1}{2}$	II	5	0.3575
0.3575	3	3	5	8	II	5	0.3574
0.3575	3	3	5	$8\frac{1}{2}$	II	5	0.3577
0.3575	3	3	5	9	II	1	0.1647
0.3575	3	3	5	$8\frac{1}{2}$	II	2	0.3143
0.3575	3	3	5	7	II	3	0.3575
0.3575	3	3	5	7	II	4	0.3573

(G) POTASSIUM CYANIDE ELECTROLYTE.

Beilstein and Jawein[1] made most satisfactory determinations of cadmium from this electrolyte, as has been done by others.[2] It was studied to some extent by Exner, and the conditions used by him, modified somewhat, were those employed in the following experiments. The addition of sodium hydroxide was necessary to decrease creeping, which was so considerable that the dilution could not exceed 100 cc. It was found that when comparatively large amounts of sodium hydroxide were used the deposits had a cloudy gray appearance, but with the minimum amount (about 1 gram), the deposit of cadmium was lustrous and of a beautiful silver-white color. In preparing the solution, potassium cyanide in excess was added first and then the sodium hydroxide. Fig. 1 shows that the rate of precipitation in this electrolyte was considerably slower than in any of the others.

[1] *Ber.*, **12**, 759.

[2] *Z. angew. Chem.*, 1892; this Journal, **19**, 870; *Z. anorg. Chem.*, **28**, 233; this Journal, **21**, 911.

TABLE IX.

$CdSO_4$ = Cd. Gram.	NaOH. Grams.	KCN. Grams.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.3565	5	4	5	4½	II	10	0.3550
0.3565	2	4	5	4½	II	15	0.3558
0.3565	3	4	5	4½	II	15	0.3568
0.3565	2	4	5	5	II	15	0.3561
0.3565	2	4	5	5	II	15	0.3566
0.3565	2	4	5	4	II	15	0.3564
0.3565	1	3	5	6	II	15	0.3563
0.3565	1	3	5	5½	II	1	0.1385
0.3565	1	3	5	5½	II	2	0.2276
0.3565	1	3	5	5½	II	3	0.2670
0.4568	1	3	5	5	II	1	0.1808
0.4568	1	3	5	5	II	2	0.2585
0.4568	1	3	5	5	II	3	0.3291
0.4568	1	3	5	5½	II	5	0.3778
0.4568	1	3	5	5	II	7½	0.4348
0.4568	1	3	5	5	II	10	0.4534
0.4568	1	3	5	5	II	15	0.4568
0.4568	1	3	5	4½	II	15	0.4578
0.4568	1	3	5	5½	II	20	0.4561
0.4568	1	3	5	5½	II	20	0.4569

The anode spiral and the cathode dish were found during these determinations to have each lost about 4 mg. in weight.

(H) AMMONIUM LACTATE ELECTROLYTE.

The results in this electrolyte were not very satisfactory, a trace of cadmium being found in the liquid siphoned off in nearly every experiment. The deposits were similar to those from other organic electrolytes.

TABLE X.

$CdSO_4$ = Cd. Gram.	NH_4OH. cc.	Lactic acid. cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.4568	4	2	5	7½	II	5	....
0.4568	12	3	5	7½	II	10	0.4647
0.4568	2	1	5	7½	II	10	0.4046
0.4568	10	5	5	7½	II	10	0.4344

(I) SODIUM LACTATE ELECTROLYTE.

Equally unsatisfactory results were obtained from this electrolyte, the last traces of metal seeming to be precipitated with great difficulty.

TABLE XI.

$CdSO_4$ =○= Cd. Gram.	NaOH. Gram.	Lactic acid. cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.4568	1	2½	5	10	II	10	0.4340
0.4045	1	3½	5	9½	II	15	0.4021
0.4045	1	3½	5	9½	II	20	0.4000
0.4045	1	5	5	8	II	20	0.4000
	Na_2CO_3. Gram.						
0.4045	1	5	5	10½	IV	15	0.4046
0.4045	1	5	5	9½	IV	2½	0.3387
0.4045	1	5	5	9½	IV	5	0.4032
0.4045	1	5	5	11	IV	7	0.4032
0.4045	1	5	5	10	IV	10	0.4042

In all these experiments a trace of cadmium was found in the liquid from the deposits.

(J) AMMONIUM SUCCINATE ELECTROLYTE.

No mention has ever been made of the deposition of cadmium from a succinate electrolyte, so that the excellent deposits of cobalt from such a solution led to its use for cadmium. The results were good, the deposits being similar to those from a formate or an acetate electrolyte. A small excess of acid was found to be desirable to insure complete precipitation. The ammonium succinate was of such a strength that 1 cc. =○= 0.2 gram succinic acid.

TABLE XII.

$CdSO_4$ =○= Cd. Gram.	Ammonium succinate. cc.	NH_4OH. cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.3996	5	.	5	9	II	10	....
0.3996	5	5	5	11½	I	12	0.3997
0.3996	5	.	5	11½	I	15	0.3995
	5 per cent. acid.						
0.3996	5	12	5	9½	V	15	0.3995
0.3996	5	10	5	10	V	12	0.3997
0.4040	5	15	5	12	IV	2	0.2830
0.4040	5	15	5	12	IV	5	0.4032
0.4040	5	15	5	11½	IV	7	0.4040
0.4040	5	15	5	11	IV	10	0.4043

(K) SODIUM SUCCINATE ELECTROLYTE.

In this electrolyte the presence of free acid was found to be undesirable. 1 cc. of the sodium succinate =○= 0.2 gram acid. The rate of precipitation is shown in Fig. 2 to be identical with

that in the ammonium succinate electrolyte. Five experiments gave the following results:

TABLE XIII.

$CdSO_4$ =○= Cd. Gram.	Sodium succinate. cc.	5 per cent. acid. cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.4040	5	15	5	11	IV	15	0.4036
0.4040	5	..	5	11	IV	15	0.4044
0.4040	5	..	5	10	IV	2	0.2885
0.4040	5	..	5	10	IV	5	0.4041
0.4040	5	..	5	9	IV	10	0.4043

The deposits were like those from ammonium succinate.

SEPARATIONS.

By the use of the high current densities, which are possible with a rotating anode, the separations, based upon differences of voltage, cannot be effected. Separations possible under these conditions are based upon the deposition or non-deposition of the separate metals from the electrolyte in which they are present together.

Ashbrook[1] described the conditions for the separation of cadmium from several metals in mineral acid electrolytes. A separation of cadmium from magnesium in a formate solution was thought to be possible, as cobalt had been separated from magnesium in this way. The following results indicate that the separation is easily accomplished.

(1) CADMIUM FROM MAGNESIUM.

TABLE XIV.

$CdSO_4$ =○= Cd. Gram.	$MgSO_4$ =○= Mg. Gram.	Na_2CO_3. Gram.	HCOOH (sp. gr. 1.06). cc.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.2660	0.1000	0.2	12	5	7	II	10	0.2662
0.2660	0.1000	0.2	12	5	6	II	10	0.2658
0.3339	0.2500	0.2	12	5	6	II	10	0.3338

It is probable also that this electrolyte would offer a separation of cadmium from the alkaline earth metals.

(2) CADMIUM FROM IRON.

The separation of these metals in a potassium cyanide electrolyte was described by Stortenbeker.[2] This method was adopted in the experiments following. Pure ferrous sulphate

[1] *Loc. cit.*

[2] *Z. Elektrochem.*, **4**, 409.

was added to the cadmium solution, acidified with sulphuric acid, potassium cyanide in excess added, and then a small quantity of sodium hydroxide necessary to prevent creeping and consequent loss. The results were as follows:

TABLE XV.

$CdSO_4$ =○= Cd. Gram.	$FeSO_4$. =○= Fe. Gram.	KCN. Grams.	NaOH. Grams.	N.D.$_{100}$ amperes.	Volts.	Speed.	Time. Minutes.	Cd found.
0.2650	0.2500	12	1	5	5	IV	20	0.2600
0.2650	0.2500	12	2	5	5	IV	20	0.2648
0.2650	0.2500	12	2	5	5	IV	25	0.2649
0.2650	0.2500	14	2	5	5	IV	25	0.2652
0.2650	0.2500	14	2	5½	5	IV	25	0.2652

In the first experiment some loss was occasioned by creeping. In the last four experiments the current was increased to 6 amperes at the end. In each of the above determinations no cadmium was found in the filtrate, and no iron in the deposit.

(3) CADMIUM FROM NICKEL.

The fact that a double cyanide solution of nickel gave no deposit even with a strong current gave rise to the hope that this separation was possible, using a rotating anode. The presence of cadmium, however, in the electrolyte caused a difference in the behavior of the nickel, and some of the latter metal was always found in the cadmium deposit. Much cadmium was always discovered in the liquid siphoned off, even after twenty minutes.

(4) CADMIUM FROM COBALT.

This separation in a double cyanide solution is mentioned,[1] and since cobalt as cobalticyanide is not deposited, even with a very strong current, the possibility of its separation from cadmium, using a rotating anode, was suggested. To a solution of potassium cobalticyanide was added a cadmium solution together with sodium hydroxide, and a current of 5–6 amperes passed through the same for twenty minutes. The resulting deposit was dark, and when dissolved off the dish with nitric acid, was found to contain no cobalt but a comparatively large quantity of insoluble particles which dissolved in aqua regia and proved to be platinum. During this experiment the platinum dish lost about 7 mg., though in a blank experiment without the cobalt no loss was sustained. In the next experiments a silvered dish was used,

[1] *Am. Chem. J.*, **12**, 104; *Z. physikal. Chem.*, **12**, 112.

with the result that the platinum was not attacked, but the cadmium was not completely precipitated even after allowing the current to pass for thirty-five minutes. This incomplete precipitation was observed in the previous experiments.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 94.]

THE RAPID DETERMINATION OF LEAD IN THE ELECTROLYTIC WAY.[1]

BY RALPH O. SMITH.

Received August 28, 1905.

IN MAKING this study it was not proposed to determine the lead as metal but as dioxide, adopting, however, the course pursued by Exner.[2]

At the very beginning care was taken to use perfectly pure lead nitrate, that there might be no question as to its metal content.

After the solution of the salt had been made, definite portions of it were removed and evaporated to dryness with sulphuric acid, and after carefully heating, the residue was weighed as lead sulphate.

Thus, 25 cc. of the stock solution of the lead nitrate gave 0.3635 gram of lead sulphate, equivalent to 0.2438 gram of metallic lead, or 0.2867 gram of lead dioxide.

To 25 cc. of this solution 20 cc. of nitric acid (sp. gr. 1.4) were added and then diluted with water to 115 cc. The solution was heated to 70° before the current was allowed to pass.

These were the conditions in each of the following experiments. The rotating electrode, which in this case was the cathode, performed about 450 revolutions a minute.

TABLE I.

Experiment.	Time. Minutes.	PbO_2 found.	Pb calculated.	Pb present.	Volts.	N.D 100 amperes.
1	3	0.2478	0.2146	0.2483	3.7	11.6–11.0
2	6	0.2679	0.2320	0.2483	3.9–3.8	10 –10.8
3	9	0.2807	0.2431	0.2483	3.8	11
4	12	0.2858	0.2475	0.2483	3.7–3.8	10.8–11
5	15	0.2873	0.2488	0.2483	3.7–3.8	11
6	18	0.2873	0.2488	0.2483	3.9	11.2–11
7	15	0.2874	0.2489	0.2483	4.0	13

[1] From the author's thesis for the Ph.D. degree.

[2] This Journal, **25**, 896.

The solutions from these experiments were siphoned off from the deposits. They were combined with the wash-water and evaporated to dryness. The residue was taken up with a little dilute acetic acid and a few drops of a potassium bichromate solution were introduced. After some hours, precipitates were observed in all the cases excepting in Expts. 5, 6 and 7. These precipitates were yellow in color and dissolved in sodium hydroxide, indicating therefore that the lead had not been completely precipitated.

A slight deposit of metallic lead was observed upon the cathode in these cases, even when 20 cc. of nitric acid were present. It is true that no perceptible increase in the weight of the cathode could be noticed, but when it was treated with a little dilute acetic acid and tested, as above indicated, traces of lead chromate were noticed. It has frequently been observed in the electrolysis of acid solutions of lead salts, that metal is precipitated upon the cathode and that it gradually dissolves as the decomposition proceeds and is deposited upon the anode as dioxide. To hasten the solution of any metal which found its way to the cathode, the current was interrupted for a short time—five seconds—about the middle of the experiment and again for a brief period before the precipitation was completed.

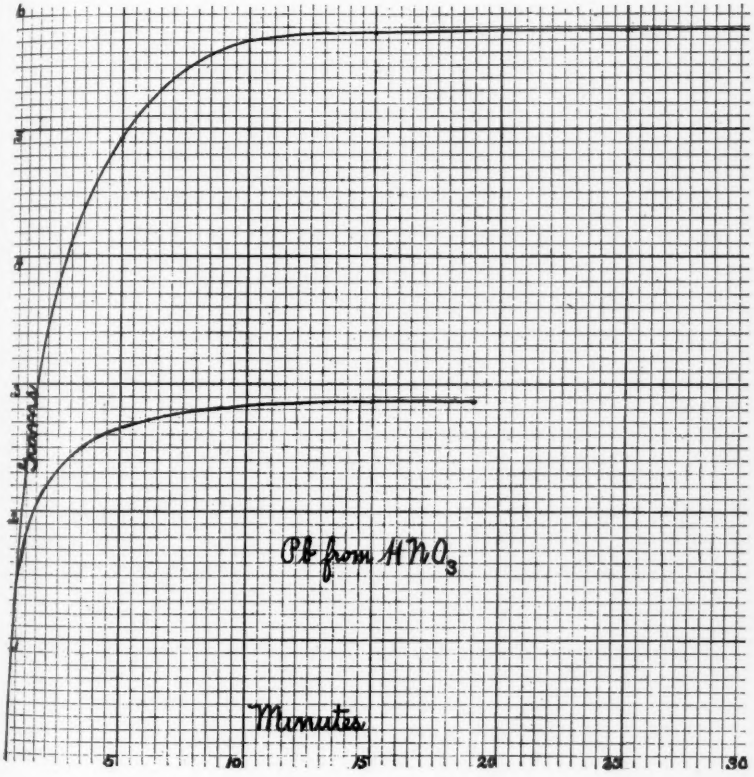
At the end of each determination the acid liquid, as previously mentioned, was siphoned off without interrupting the current, fresh water being introduced to keep the level above the deposit until the ammeter stood at zero. The current was then interrupted, the dish removed, and its contents washed with absolute alcohol and with absolute ether. It was dried to constant weight at 230° C. and allowed to cool in a desiccator for fifteen minutes, when it was weighed. The deposit did not alter in weight after standing in the balance for two hours. It was removed from the dish with a mixture of oxalic and nitric acids.

In the next series of experiments the conditions were the same as those which prevailed in the first series with the exception that 50 cc. of the lead nitrate solution, equivalent to 0.4996 gram of lead, were used. The results were as follows:

TABLE II.

Experiment.	Time. Minutes.	PbO_2 found.	Pb found.	Pb present.	Volts.	N.D 100 amperes.
8	5	0.4940	0.4279	0.4996	4	11
9	10	0.5708	0.4944	0.4996	4 –3.9	11
10	15	0.5747	0.4978	0.4996	3.9–3.8	11 –10.9
11	20	0.5770	0.4997	0.4996	4 –3.6	11.1–11
12	25	0.5787	0.5012	0.4996	3.8–3.5	11.2–11
13	30	0.5789	0.5014	0.4996	3.6–3.7	11.2–10.8

The time-curve exhibited in the plate was constructed from the results presented in these two series. The residual liquids from the deposits were, with the exception of those in Expts. 12 and 13, found to contain traces of lead.



Rate of deposition of lead dioxide.

It will be seen from the series just presented that the maximum time period for a quarter of a gram of metal is fifteen minutes, and the maximum time for half a gram of metal is twenty-five minutes. It will be further noticed that the amount of lead calculated from the deposits is too large by 0.005 gram in the former case, and 0.0016 to 0.0018 gram in the latter.

To make sure that the preceding deductions were correct and to learn how far the method was accurate, a third series of experiments was conducted, different weights of material being used. Again the amount of lead in the nitrate was first determined as sulphate. The electrolyte and the conditions of electrolysis were the same as in the preceding experiments. The results of this third series were as follows:

TABLE III.

Experiment.	Time. Minutes.	PbO_2 found.	Pb calculated.	Pb present.	Error. Mg.	Error. Per cent.	Volts.	N.D$_{100}$ amperes.
12	25	0.5787	0.5021	0.4996	+1.6	+0.32	3.8–3.5	11.2–11
13	30	0.5789	0.5014	0.4996	+1.8	+0.36	3.6–3.7	11.2–10.8
14	25	0.5781	0.5007	0.4992	+1.5	+0.30	4 –3.6	11.3–11.2
15	30	0.5780	0.5006	0.4992	+1.4	+0.28	3.6	11
5	15	0.2873	0.2488	0.2483	+0.5	+0.20	3.7–3.8	10.8–11
6	18	0.2873	0.2488	0.2483	+0.5	+0.20	3.9	11.2–11
7	15	0.2874	0.2489	0.2483	+0.6	+0.24	4	13
16	15	0.2885	0.2499	0.2496	+0.3	+0.12	3.8–3.7	11
17	20	0.2889	0.2502	0.2496	+0.6	+0.24	3.8	11
18	180	0.2887	0.2501	0.2496	+0.5	+0.20	2.3–2.1	1.6– 1.5
19	15	0.1137	0.0985	0.0982	+0.3	+0.26	3.8–3.7	11 –11.2
20	16	0.1136	0.0984	0.0982	+0.2	+0.17	4 –3.7	11.4
21	17	0.0567	0.0491	0.0491	±0.0	±0.00	4 –3.7	11.5–11
22	16	0.0563	0.0488	0.0491	—0.3	±0.61	3.9–3.8	11.4–10.8
23	15	0.0569	0.0493	0.0491	+0.2	+0.41	3.9–3.6	11.2–11
24	15	0.0565	0.0489	0.0491	—0.2	—0.41	4 –3.6	11 –10.9
25	15	0.0567	0.0491	0.0491	±0.0	±0.00	3.8–3.6	11.2–11

It is plain that the results of determinations of different amounts of lead agree very well for each definite weight, but it will be discovered on turning to column 6, beginning with the smallest deposit of lead dioxide, that the lead equivalents are too high, and that the error grows gradually with the weight of the deposits until in the case of those approximating 0.58 gram of lead dioxide the lead equivalent is on the average 1.5 mg. too high. This is exactly the opposite of what Hollard[1] observed. He used station-

[1] *Ann. de Chim. Anal.*, 4, 11.

ary electrodes and dried the deposits at 200° C. for a period of fifteen minutes.

In Expt. 18 the cathode was stationary, and the result is in close agreement with the others of its class. It is of interest to note the effect of the increase of temperature upon this deposit.

TABLE IV.

Minutes heated.	Temperature.	Weight of deposit.
30	180–190°	0.2895
30	180–190°	0.2895
15	230°	0.2889
15	230°	0.2887
120	230°	0.2887

These changes led to a study of the weights of all the deposits at different temperatures: 180–190° (Classen), at 200° for fifteen minutes (Hollard), and finally to constant weight at 230°, an idea taken from the work of Carnelly and Walker.[1]

TABLE V.

Experiment.	Minutes heated.	Temperature.	Weight of deposit.	Pb present.	Pb/PbO_2 factor.
12	30	180–190°	0.5805		
	90	180–190°	0.5805		
	30	190–210°	0.5799		
	120	190–210°	0.5799		
	30	240°	0.5787		
	180	240°	0.5787	0.4996	0.8633
13	60	240°	0.5789		
	30	240°	0.5789	0.4996	0.8630
14	30	200°	0.5788		
	30	200°	0.5788		
	30	240°	0.5781		
	30	240°	0.5781	0.4992	0.8635
15	30	200°	0.5788		
	30	200°	0.5790		
	30	230°	0.5780		
	120	240°	0.5780	0.4992	0.8635
				Average,	0.8634

The weights of these deposits were not changed by further drying for two hours at 270° C., and consequently show that deposits of lead dioxide approximating 0.5 gram in weight do not really have a constant composition until they have been dried at 230° C.

[1] *J. Chem. Soc.* (London), **53**, 85.

Deposits of lead dioxide approximating 0.288 gram in weight were heated at different temperatures with the following results:

TABLE VI.

Experiment.	Minutes heated.	Temperature.	Weight of deposit.	Pb present.	Pb/PbO_2 factor.
5	15	230°	0.2878		
	60	230°	0.2873		
	60	230°	0.2873	0.2483	0.8641
6	30	230°	0.2873	0.2483	0.8641
7	60	200–220°	0.2874		
	40	230–250°	0.2873		
	140	240°	0.2874	0.2483	0.8640
16	30	200°	0.2885		
	30	200°	0.2885		
	30	230°	0.2885		
	30	230°	0.2885	0.2496	0.8651
17	30	200°	0.2889		
	30	200°	0.2889		
	30	230°	0.2889	0.2496	0.8640
18	See Table IV.		0.2887	0.2496	0.8646
					Average, 0.8643

It is evident that this quantity of lead dioxide reaches a constant weight when dried at 200°, and that this condition is reached only after it has been exposed to that temperature for more than a half hour.

When the quantity of the lead dioxide deposit is small, say from 0.05 to 0.1 gram, it is hardly necessary to introduce an analytical factor.

The following experiments show the weights of such smaller deposits (1) after washing with absolute alcohol and absolute ether and (2) after they have been dried at 230° to constant weight. They further indicate that there is little probability of the formation of a definite hydrated lead dioxide in such cases.

TABLE VII.

Experiment.	(1).	(2).	Loss.
19	0.1147	0.1137	0.0010
20	0.1150	0.1136	0.0014
21	0.0570	0.0567	0.0003
22	0.0567	0.0563	0.0004
23	0.0569	....	....
24	0.0573	0.0565	0.0008
25	0.0569	0.0567	0.0002

It may be fairly concluded from the preceding experiments that deposits of lead dioxide made in the electrolytic way will be too high unless they have been dried for definite periods at a temperature ranging from 200° to 230° C. Much depends upon the weight of the deposits, but an analytical factor will be necessary.

It is not probable that the excessive weight of the deposits is due to the formation and precipitation of a higher oxide of lead than the dioxide. It is more likely, as is evidenced by Schucht's[1] work also, that the final traces of water, adhering or included, are expelled with difficulty. The fact that the error increases with the density of the deposit might be advanced as an argument in favor of this view.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 109.]

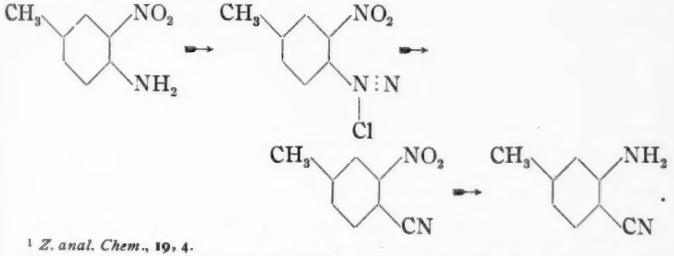
SOME ACYL DERIVATIVES OF HOMOANTHRANILIC NITRILE, AND THE 7-METHYL-4-KETODIHYDROQUINAZOLINES PREPARED THEREFROM.[2]

BY MARSTON TAYLOR BOGERT AND ALFRED HOFFMAN.

Received August 1, 1905.

IN A previous paper, Bogert and Hand[3] have shown that quinazolines can be very easily obtained from anthranilic nitrile. In the present paper, the method is applied to homoanthranilic nitrile with equally successful results.

Homoanthranilic nitrile was prepared from *m*-nitro-*p*-toluidine by converting the latter into *m*-nitro-*p*-tolunitrile by the Sandmeyer reaction, and then reducing the nitro group with stannous chloride and hydrochloric acid:

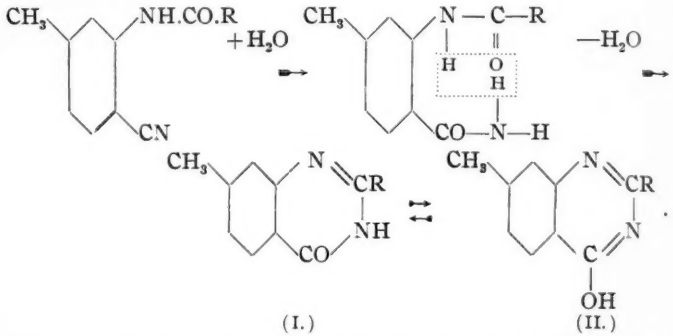


[1] *Z. anal. Chem.*, **19**, 4.

[2] Read before the New York Section of the American Chemical Society, May 5, 1905.

[3] This Journal, **24**, 1031 (1902).

Various acyl derivatives of homoanthranilic nitrile were prepared, which were then converted into quinazolines by heating them with alkaline hydrogen dioxide solution, as described by Bogert and Hand:[1]



(I.) (II.)

While the free quinazolines may exist in the keto condition (I), their alkaline salts quite certainly possess the enol structure (II).

Several of the quinazolines described in this paper have been previously reported by Niementowski,[2] who obtained them by heating either homoanthranilic acid with an amide, or homoanthranilamide with an acid. Both homoanthranilic acid and its amide he prepared from the nitrile. Our process permits of the preparation of the quinazolines directly from the acylated nitriles, without the isolation of the amides; and, further, as we have elsewhere shown,[3] thioquinazolines may be obtained from these aminonitriles with equal facility.[4]

EXPERIMENTAL.

m-Nitro-p-Tolunitrile, (1) $CH_3.C_6H_3\begin{matrix}NO_2\ (3)\\ CN\ (4)\end{matrix}$, was prepared from *m*-nitro-*p*-toluidine, by the Sandmeyer reaction, in exactly the same way as *o*-nitrobenzonitrile was prepared by Bogert and Hand[1] from *o*-nitraniline. The addition of a few drops of ether from time to time during the diazotizing materially assisted the reaction, by causing the solution of the diazonium body. The

[1] *Loc. cit.*

[2] *J. prakt. Ch.* [2], **40**, 12 (1889); **51**, 566 (1895); *Ber.*, **27**, 516 (1894).

[3] This Journal, **25**, 372, 935 (1903).

[4] A paper will appear later upon the thioquinazolines derived from homoanthranilic nitrile.

diazotizing was carried out at 33°, and was complete in three to four hours. When ether was used, there resulted a perfectly clear purple solution, while, in absence of ether, the solution was dark brown, and considerable of the diazonium body remained undissolved as a flocculent precipitate. The yield of pure nitronitrile was 80 per cent. of the theoretical. The pure substance crystallizes from water in nearly colorless needles, of a slight greenish cast, and melts at 99.8° (corr.).

Homoanthranilic Nitrile, (1) $CH_3.C_6H_3\begin{cases}NH_2\ (3)\\CN\ (4)\end{cases}$.—*m*-Nitro-*p*-tolunitrile was reduced to the corresponding aminonitrile, by stannous chloride and hydrochloric acid, as follows:

Five hundred grams stannous chloride were dissolved in 425 cc. concentrated hydrochloric acid, and 75 cc. water added. The solution was heated to 50°, and stirred vigorously with a turbine. 108.9 grams of the nitronitrile were added gradually, at such a rate that the temperature remained at 50–55°. When the reduction was complete, a clear solution resulted. An equal volume of alcohol was then added, a concentrated solution of 340 grams sodium hydroxide slowly stirred in, and the mixture finally made alkaline with ammonium hydroxide. A large amount of alcohol was then poured in, and the mixture left several hours to settle. The clear alcoholic solution of the nitrile was decanted through a filter, and the precipitated metastannic acid washed several times with alcohol, the washings being added to the first filtrate. The alcoholic solution was distilled down until it turned a deep red, and the nitrile was then precipitated by the addition of a large volume of water. The precipitate, after being washed with water (to remove ammonium chloride), was quite pure. It was further purified by crystallization from carbon disulphide in presence of bone-black. Small amounts of homoanthranilic acid and its amide are frequently formed in the reduction, but do not interfere, and are found in the mother-liquors from the nitrile crystals. The yield of aminonitrile was 80 per cent. of the theoretical.

The pure aminonitrile crystallizes from carbon disulphide in beautiful, large, yellowish crystals, melting at 94° (corr.).

The Preparation of Acyl Derivatives of Homoanthranilic Nitrile.—With the exception of the formyl compound, the aliphatic acyl

derivatives were all prepared by heating the aminonitrile with the acid anhydride, and crystallizing the product from a suitable solvent. In the case of the aromatic acids, the acid chloride and the aminonitrile were dissolved in separate portions of pyridine, the solutions carefully mixed, and the acyl derivative then precipitated by adding water.

Formyl Homoanthranilic Nitrile, (1) $CH_3.C_6H_3\begin{cases}NH.COH\ (3)\\CN\ (4)\end{cases}$.

—All attempts to prepare this derivative failed, the product in every case being the quinazoline. Apparently the formyl derivative is so unstable that it rearranges spontaneously to the quinazoline. Niementowski[1] experienced the same difficulty in the preparation of the formyl derivative of homoanthranilamide, which invariably passed over into the quinazoline by loss of water.

Acetyl Homoanthranilic Nitrile, (1) $CH_3.C_6H_3\begin{cases}NH.CO.CH_3\ (3)\\CN\ (4)\end{cases}$.

—Four grams of homoanthranilic nitrile were dissolved in 5 cc. of acetic anhydride, the solution boiled gently for two hours, poured into water, the precipitate crystallized from dilute acetic acid, and then from alcohol. It then appeared in colorless needles, m. p. 136° (corr.), identical with the product described by Niementowski.[2] It is easily soluble in alcohol, acetone, or chloroform; moderately soluble in benzene or ether; difficultly soluble in carbon disulphide, amyl alcohol, or gasoline.

	Calculated for $C_{10}H_{10}ON_2$.	Found.
Nitrogen.....	15.96	16.3

Propionyl Homoanthranilic Nitrile, (1) $CH_3.C_6H_3\begin{cases}NH.CO.C_2H_5(3)\\CN\ (4)\end{cases}$,

prepared from homoanthranilic nitrile and propionic anhydride, was crystallized from dilute propionic acid and then from alcohol. It forms colorless needles, m. p. 138° (corr.), showing approximately the same solubilities as the acetyl derivative in acetic acid, ethyl or amyl alcohols, acetone, chloroform, benzene, ether, carbon disulphide, or gasoline.

[1] *J. prakt. Chem.* [2], **51**, 566 (1895).
[2] *Ibid.*, [2], **40**, 8 (1889).

	Calculated for $C_{11}H_{12}ON_2$.	Found.	
Carbon	70.2	69.9	70.08
Hydrogen	6.4	6.3	6.26
Nitrogen	14.9	15.3	15.5

Isobutyryl Homoanthranilic Nitrile,

(1) $CH_3.C_6H_3\begin{cases}NH.CO.CH(CH_3)_2\ (3)\\CN\ (4)\end{cases}$, from homoanthranilic nitrile and isobutyric anhydride, crystallizes from alcohol in colorless needles, m. p. 144° (corr.); easily soluble in benzene, acetic acid, acetone, chloroform, or hot alcohol; moderately soluble in cold alcohol, hot carbon disulphide or amyl alcohol; difficultly soluble in cold carbon disulphide, cold amyl alcohol, or gasoline.

	Calculated for $C_{12}H_{14}ON_2$.	Found.
Nitrogen	13.9	13.7

Isovaleryl Homoanthranilic Nitrile,

(1) $CH_3.C_6H_3\begin{cases}NH.CO.CH_2.CH(CH_3)_2\ (3)\\CN\ (4)\end{cases}$, from homoanthranilic nitrile and isovaleric anhydride, crystallizes from alcohol in small colorless needles, m. p. 139° (corr.); easily soluble in benzene, carbon disulphide, acetone, acetic acid, ether, ethyl or amyl alcohols, chloroform, or hot gasoline; moderately soluble in cold gasoline.

	Calculated for $C_{13}H_{16}ON_2$.	Found.
Nitrogen	13.00	13.28

Benzoyl Homoanthranilic Nitrile, (1) $CH_3.C_6H_3\begin{cases}NH.CO.C_6H_5\ (3)\\CN\ (4)\end{cases}$, from homoanthranilic nitrile and benzoyl chloride, in pyridine solution, crystallizes from benzene in fine white needles, m. p. 145° (corr.); easily soluble in cold chloroform, or hot benzene, in carbon disulphide, ethyl or amyl alcohols, acetone, or acetic acid; difficultly soluble in ether or gasoline.

	Calculated for $C_{15}H_{12}ON_2$.	Found.
Nitrogen	11.8	11.9

m-Nitrobenzoyl Homoanthranilic Nitrile,

(1) $CH_3.C_6H_3\begin{cases}NH.CO.C_6H_4.NO_2(m)\ (3)\\CN\ (4)\end{cases}$, from *m*-nitrobenzoyl chlo-

ride and homoanthranilic nitrile, in pyridine solution, crystallizes in a finely felted mass of colorless needles, m. p. 218° (corr.); easily soluble in cold acetone, or hot benzene, in chloroform, ethyl or amyl alcohols, or acetic acid; difficultly soluble in ether, carbon disulphide, or gasoline.

	Calculated for $C_{15}H_{11}O_3N_3$.	Found.
Nitrogen..	14.9	14.98

p-Nitrobenzoyl Homoanthranilic Nitrile,

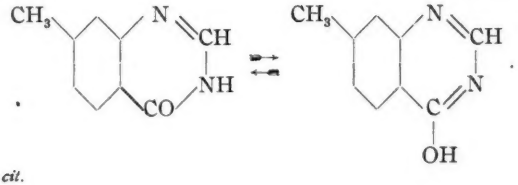
(1) $CH_3.C_6H_3\begin{cases}NH.CO.C_6H_4.NO_2\ (p)\ (3)\\ CN\ (4)\end{cases}$, from homoanthranilic nitrile and *p*-nitrobenzoyl chloride, in pyridine solution, melts at 223° (corr.), and resembles the meta isomer in appearance. It is easily soluble in hot alcohol, acetic acid, amyl alcohol, or acetone; moderately soluble in hot benzene, or chloroform; difficultly soluble in carbon disulphide, ether, or gasoline.

	Calculated for $C_{15}H_{11}O_3N_3$.	Found.
Nitrogen.....	14.9	15.04

The Preparation of Quinazolines from Acyl Homoanthranilic Nitriles.

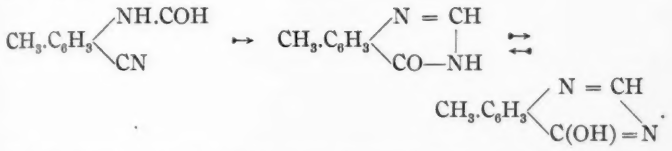
The acyl homoanthranilic nitriles were heated with a mixture of equal parts 10 per cent. aqueous potassium hydroxide solution and commercial (approximately 3 per cent.) hydrogen dioxide solution. The yield of quinazoline was excellent in most cases. These quinazolines dissolve in caustic alkalies, or in strong mineral acids, the former solution being precipitated by carbon dioxide, the latter by ammonia. Of the quinazolines described, the isobutyl, phenyl, *m*- and *p*-nitrophenyl derivatives are new; the others have been prepared by Niementowski[1] from homoanthranilic acid or its amide.

7-Methyl-4-ketodihydroquinazoline (*7-methyl-4-hydroxyquinazoline*),



[1] *Loc. cit.*

—As already stated, all efforts to prepare formyl homoanthranilic nitrile resulted in the formation of the quinazoline by rearrangement:



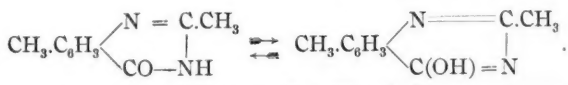
When glacial formic acid and homoanthranilic nitrile reacted, even at low temperature, the product was the quinazoline. It was purified by solution in boiling hydrochloric acid, reprecipitating with ammonia, washing the precipitate thoroughly with water, and subliming. A mass of fluffy crystals resulted, melting at 239° (corr.), and similar to the compound described by Niementowski.[1]

To make certain of the identity of our product with Niementowski's, we prepared some of the quinazoline by the latter's method. Homoanthranilamide was obtained by boiling 4 grams of the nitrile with 80 cc. of water and 2 grams of potassium hydroxide until a clear solution resulted. On cooling, the amide separated in crystals. It was filtered out, washed with water, and recrystallized from alcohol, when it melted sharply at 146°. To make the quinazoline, 2 grams of the amide were boiled with 0.5 cc. of formic acid for half an hour, when the mass suddenly solidified. The product, washed with water and sublimed, proved to be identical in all respects with the quinazoline obtained from the nitrile. Niementowski[1] also obtained this quinazoline by the action of formamide upon homoanthranilic acid.

The sublimed quinazoline forms colorless needles, m. p. 239° (corr.); apparently insoluble in water, carbon disulphide, ether, chloroform, or mixtures of these; slightly soluble in benzene, glacial acetic acid, or amyl alcohol; easily soluble in aniline or phenol. It forms a crystalline hydrochloride, which is quite easily dissociated by water, and a crystalline chlorplatinate.

2,7-Dimethyl-4-ketodihydroquinazoline (*2,7-Dimethyl-4-hydroxyquinazoline*),

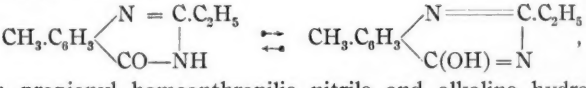
[1] *Loc. cit.*



—1.5 grams of acetyl homoanthranilic nitrile were warmed at 40–50° for two hours with 50 cc. 10 per cent. potassium hydroxide solution and 50 cc. commercial 3 per cent. hydrogen dioxide solution, when a clear solution of the potassium salt of the quinazoline resulted. This solution was acidified with hydrochloric acid, and ammonium hydroxide then added in excess. The precipitated quinazoline was crystallized from alcohol, giving fine fluffy needles, m. p. 255° (corr.); easily soluble in acetone, ethyl or amyl alcohols, acetic acid, or hot chloroform; difficultly soluble in benzene, gasoline, ether, or carbon disulphide. It is identical with the product obtained by Niementowski[1] from homoanthranilic acid and acetamide.

	Calculated for $C_{10}H_{10}ON_2$.	Found.
Nitrogen	15.96	16.12

2-Ethyl-7-methyl-4-ketodihydroquinazoline (*2-Ethyl-7-methyl-4-hydroxyquinazoline*),



from propionyl homoanthranilic nitrile and alkaline hydrogen dioxide solution, crystallizes in felted needles, m. p. 240° (corr.); easily soluble in alcohol, chloroform, acetic acid, hot benzene, hot acetone, or hot amyl alcohol; difficultly soluble in gasoline, ether, or carbon disulphide.

	Calculated for $C_{11}H_{12}ON_2$.	Found.	
Carbon	70.2	70.7	69.3
Hydrogen	6.4	6.4	6.4
Nitrogen	14.9	14.81	.....

The compound was first described by Niementowski.[1]

2-Isopropyl-7-methyl-4-ketodihydroquinazoline (*2-Isopropyl-7-methyl-4-hydroxyquinazoline*), from isobutyryl homoanthranilic nitrile and alkaline hydrogen dioxide solution, crystallizes in felted needles, m. p. 228° (corr.); easily soluble in alcohol, acetic acid, hot benzene, acetone, or amyl alcohol; moderately soluble in gasoline, ether, or chloroform; difficultly soluble in carbon disulphide.

[1] *Loc. cit.*

	Calculated for $C_{12}H_{14}ON_2$.	Found.
Nitrogen	13.9	13.97

This quinazoline also has been previously described by Niementowski.[1]

The following quinazolines were prepared from the corresponding acyl homoanthranilic nitriles and alkaline hydrogen dioxide solution, as just described.

2-Isobutyl-7-methyl-4-ketodihydroquinazoline (*2-Isobutyl-7-methyl-4-hydroxyquinazoline*). — Felted needles, m. p. 219° (corr.); easily soluble in acetone, acetic acid, hot benzene, carbon disulphide, chloroform, ethyl or amyl alcohols; difficultly soluble in gasoline.

	Calculated for $C_{13}H_{16}ON_2$.	Found.
Nitrogen	13.00	13.3

2-Phenyl-7-methyl-4-ketodihydroquinazoline (*2-Phenyl-7-methyl-4-hydroxyquinazoline*) crystallizes either in needles or plates, both of which forms melt at 243° (corr.). It is easily soluble in chloroform, hot benzene, ethyl or amyl alcohols, or acetic acid; difficultly soluble in carbon disulphide, acetone, gasoline, or ether.

	Calculated for $C_{15}H_{12}ON_2$.	Found.
Nitrogen	11.8	11.95

2-m-Nitrophenyl-7-methyl-4-ketodihydroquinazoline (*2-m-Nitrophenyl-7-methyl-4-hydroxyquinazoline*). — Microcrystalline powder, melting sharply above 370°; easily soluble in acetone, chloroform, hot amyl alcohol, acetic acid, or ethyl alcohol; difficultly soluble in benzene, carbon disulphide, gasoline, or ether. In contradistinction to the foregoing quinazolines, it is not easily soluble either in mineral acids or caustic alkalies.

	Calculated for $C_{15}H_{11}O_3N_3$.	Found.
Nitrogen	14.9	15.03

2-p-Nitrophenyl-7-methyl-4-ketodihydroquinazoline (*2-p-Nitrophenyl-7-methyl-4-hydroxyquinazoline*) melts sharply above 370°, and in general appearance and properties closely resembles the above meta isomer.

	Calculated for $C_{15}H_{11}O_3N_3$.	Found.
Nitrogen	14.9	14.6

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
April, 1905.

[1] *Loc. cit.*

[Contributions from the Havemeyer Laboratories of Columbia University, No. 110.]

THE CONDENSATION OF SUCCINYLOSUCCINIC ACID DIETHYL ESTER WITH ACETAMIDINE: 2,6-DIMETHYL-4,8-DIHYDROXY-9,10-DIHYDRO-1,3,5,7-NAPHTOTETRAZINE.[1]

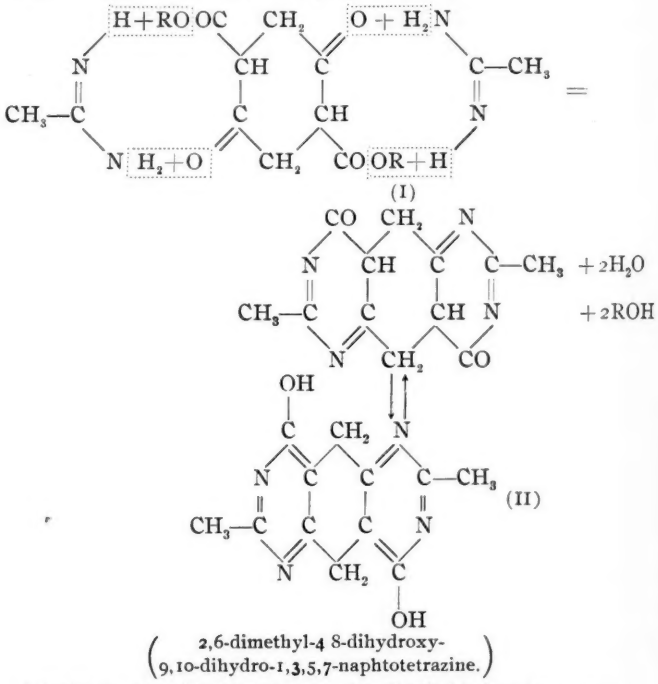
By Marston Taylor Bogert and Arthur Wayland Dox.

Received August 10, 1905.

In a previous paper,[2] we have described the preparation of a naphtotetrazine from succinylosuccinic ester and guanidine.

As the condensation there described depends upon the amidine structure of guanidine, it was expected that other amidines would react similarly, and we have found that acetamidine and succinylosuccinic ester condense smoothly to a naphtotetrazine.

The condensation may be represented thus:

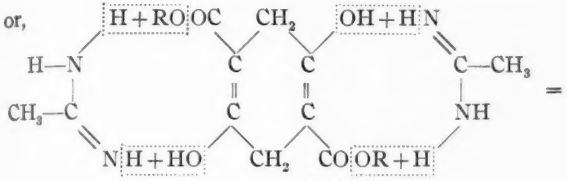


2,6-dimethyl-4 8-dihydroxy-9,10-dihydro-1,3,5,7-naphtotetrazine.

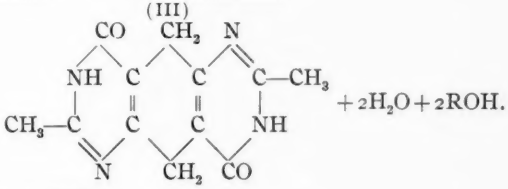
[1] Read at the General Meeting of the American Chemical Society, June 22, 1905.

[2] This Journal, **27**, 1127.

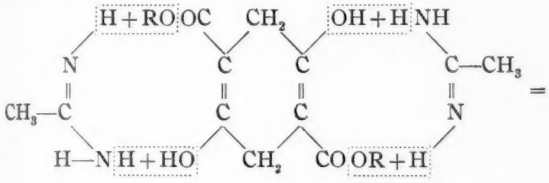
or,



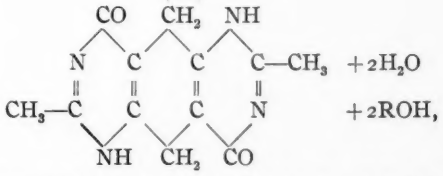
(III)



There is another possibility:



(IV)



but this appears much less probable, in view of the ready solubility of the product in alkali.

Since both I and III would pass into the same enol form (II), it is reasonably certain that this is the structure of the sodium salt. If the free base exists in the keto condition, it may then be either I or III.

The study of these new heterocycles will be continued.

EXPERIMENTAL.

The Condensation of Succinylosuccinic Ester with Acetamidine.—The condensation was at first conducted in exactly the same manner as with guanidine.[1] The yields were small, owing to the

[1] *Loc. cit.*

instability of the liberated acetamidine, most of the latter probably being decomposed before condensation with the succinylosuccinic ester occurred. By using the sodium salt of the ester, however, it was found possible not only to secure the condensation at the ordinary temperature, but also to increase the yield considerably.

The sodium salt of succinylosuccinic ester was dissolved in the smallest possible amount of cold water, the solution made slightly alkaline, and acetamidine hydrochloride added. After shaking for two or three minutes, needle-shaped crystals began to separate, and after standing for an hour the reaction was complete. The mother-liquor was reddish in color.

The free base was purified, as in the case of the guanidine condensation product, by crystallization of its sodium salt. The purified sodium salt was dissolved in hot water, and the calculated amount of acid added. The free base separated as a white precipitate, easily soluble in excess of mineral acid. It dissolves in ammonium hydroxide with a blue fluorescence, but is insoluble in the usual neutral organic solvents. When heated, it chars without melting, and without evolving any ammonia. No chlorplatinate could be formed.

The analysis of the free base resulted as follows:

	Calculated for $C_{12}H_{12}O_2N_4$.	Found.	
Carbon	59.02	58.90	
Hydrogen	4.92	4.83	
Nitrogen	22.95	23.00	23.12

Sodium Salt, $C_{12}H_{10}O_2N_4Na_2.6H_2O$.—The crude sodium salt was purified by recrystallization from caustic soda, as described for the guanidine condensation product. It forms colorless needles, which dissolve in hot water without the addition of alkali. The solution is colorless, but has a strong blue fluorescence. On heating, the salt chars, gives off ammonia, and leaves a residue of sodium carbonate. Like the corresponding guanidine condensation product, the crystals from caustic soda carry six molecules of water. The determination of the water of crystallization resulted as follows:

	Calculated for $C_{12}H_{10}O_2N_4Na_2.6H_2O$.	Found.	
		I.	II.
H_2O	27.27	27.12	27.27

Sodium was determined in the dried salt with the following results:

	Calculated for $C_{12}H_{10}O_5N_4Na_2$.	Found. I.	Found. II.
Na	15.97	15.75	15.80

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
June, 1905.

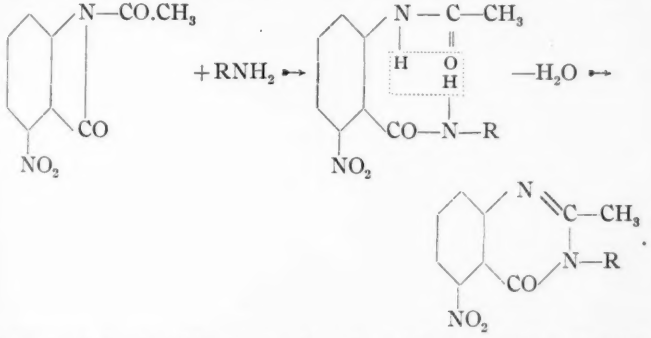
[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 111.]

THE SYNTHESIS OF 2-METHYL-5-NITRO-4-KETODIHYDROQUINAZOLINES FROM 6-NITROACETANTHRANIL AND PRIMARY AMINES.[1]

BY MARSTON TAYLOR BOGERT AND HARVEY AMBROSE SEIL.

Received August 21, 1905.

IN a previous paper,[2] Bogert and Chambers have shown that quinazolines can be readily obtained from 6-nitroacetanthranil and primary amines, the reactions involved being as follows:



They carried out this synthesis only with ammonia and with aniline. The present paper records similar syntheses with the following primary amines—methyl, ethyl, normal and isopropyl, iso- and secondary butyl, isoamyl and allyl—thus demonstrating the general applicability of the reaction to primary aliphatic amines.

We are now engaged in extending the reaction to other primary amino compounds, including the amino acids, and have already

[1] Read at the Meeting of the New York Section of the American Chemical Society, May 5, 1905.

[2] This Journal, **27**, 649 (1905).

secured some very interesting results which will be communicated in the near future.

We have experimented with some of the other nitroacetanthranils and find that they exhibit a similar behavior with primary amines. Papers upon these are in preparation.

It will be seen, from the above exhibition of the reaction, how a primary amine condenses with the nitroacetanthranil to form a quinazoline, and that this condensation is entirely independent of the character of "R." Our experiments to date indicate that almost any primary amino group can thus be converted into a nitroquinazoline cycle. The interesting synthetic field thus opened is obvious. But it is not unlikely that the reaction may have analytical value also, by affording a means of changing an unstable or liquid primary amino compound into a stable crystalline nitroquinazoline which can be easily identified.

The condensation of acylanthranils and primary amines to quinazolines was discovered by Anschütz, Schmidt and Greiffenberg.[1] They used unsubstituted acylanthranils, which we think are not so easily prepared or so reactive as the nitro derivatives.

The intermediate products in the above synthesis, the nitroacylanthranilamides, have been isolated in several cases, and then in turn changed to quinazolines, thus demonstrating experimentally the course of the reaction.

EXPERIMENTAL.

Preparation of 6-Nitroacetanthranil.

The preparation of this compound was carried out in approximately the same way as already described by Bogert and Chambers[2] from 3-nitrophthalic acid, through the nitrophthalimide, nitrophthalamic acid, and nitroanthranilic acid.

In the preparation of the nitrophthalimide, some additional experiments were made which may be of value to other workers in the same field. The following methods of preparation were compared:

(1) The action of ammonia gas upon the fused anhydride.[3]

(2) Heating the acid ammonium salt.[4]

(3) Heating the neutral ammonium salt.

[1] *Ber.*, **35**, 3480 (1902).
[2] *Loc. cit.*
[3] Kahn: *Ber.*, **35**, 3866 (1902).
[4] Bogert and Chambers: *Loc. cit.*

(4) Adding excess of ammonia to the acid methyl ester, evaporating to dryness, and fusing the residue.

The first of these methods proved the least satisfactory, both as to yield and quality of product. The others all gave good yields and good products. The advantage of the third and fourth methods is that an excess of ammonia can be used and the preparation of a pure acid salt thus obviated. As the 3-nitrophthalic acid is frequently separated from the isomeric 4-nitro acid by conversion into its acid methyl ester, the application of the fourth method is evident.

The third and fourth methods are carried out in much the same way. The acid, or acid ester, is treated with an excess of ammonia and evaporated to dryness at 110°. The temperature is then raised to 170–180° until no more ammonia is evolved, and then to 210° until fusion occurs. When the fused mass has ceased to effervesce, the temperature is raised for a few minutes to 216°, and the melt is then allowed to cool. The crude imide from the acid methyl ester forms large, yellow lustrous needles, melting sharply at 216°, and is practically pure. That from the neutral ammonium salt melts at 210–216°, but is easily purified by crystallization from alcohol.

Preparation of Quinazolines from 6-Nitroacetanthranil.

The general method of procedure was as follows: Five grams of the nitroacetanthranil were placed in a flask with a slight excess of an aqueous (1 : 3) solution of the primary amine. Considerable heat was evolved (the reaction with the pure amine was generally too violent), and the solution became colored. This color varied from a yellow with methylamine, to a red with isoamylamine. When the first reaction was over, the flask was heated two or three minutes on a steam-bath, and then allowed to cool. Most of the quinazoline separated as a precipitate in the flask, contaminated with some of the intermediate amide. The mixture was made slightly acid with acetic acid and filtered. The precipitate of quinazoline was freed from amide by washing it with cold dilute caustic potash, and the alkaline washings were added to the mother-liquor. The combined mother-liquor and alkaline washings should be slightly alkaline (too strong alkali gives a deep red color). By boiling this alkaline solution, all amide was changed to quinazoline and precipitated at once. This precipitate was

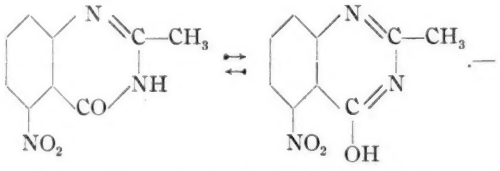
combined with the first crop of quinazoline, and the two purified together by crystallization from alcohol. The total yield in most cases was nearly quantitative.

The following method of converting the amide into quinazoline was also tried: After the completion of the reaction between the anthranil and the amine, the mixture was evaporated to dryness at 100°. The temperature was then raised to 150° and kept there until the cessation of all effervescence (about four hours), when it was allowed to cool. There resulted a brown cake, from which the pure quinazoline was obtained only after frequent recrystallizations from alcohol in the presence of boneblack. The yield also was poor.

Weddige[1] has shown that acylanthranilamides pass into quinazolines on boiling with water or with alkalies, or when fused.

These quinazolines are all white crystalline solids, of high melting-points. The allyl derivative is dimorphous. All, except the quinazoline obtained with ammonia, carry hydrocarbon radicals in positions 2 and 3, and are, therefore, insoluble in alkalies. In general, they are all insoluble, or difficultly soluble, in water, carbon tetrachloride, carbon disulphide, petroleum ether, cold benzene or cold ether; moderately soluble in the two latter solvents at the boiling-point, or in cold methyl, ethyl or amyl alcohols, or in cold acetone; easily soluble in the four latter solvents at the boiling-point, and in chloroform, or ethyl acetate. Beautiful crystals may be secured by dissolving the quinazoline in a slight excess of boiling strong alcohol, adding water carefully to the hot solution until it begins to cloud, and then allowing the solution to cool.

2-Methyl-5-nitro-4-ketodihydroquinazoline (*2-Methyl-5-nitro-4-oxyquinazoline*),



This was prepared from the nitroacetanthranil and ammonia, as already described by Bogert and Chambers.[2] As it contains a

[1] *J. prakt. Chem.* [2], **31**, 124 (1885); **36**, 141 (1887).
[2] *Loc. cit.*

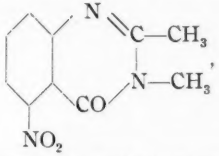
replaceable (enolic) hydrogen, it dissolves freely in alkalies. It is also moderately soluble in water. In these respects, it differs from the quinazolines which follow:

6-*Nitroacetanthranilamide*,

(6) $O_2N.C_6H_3\begin{cases}CO.NH_2\ (1)\\NH.CO.CH_3\ (2)\end{cases}$.—

This is the intermediate product in the above condensation, and was isolated in one of the experiments. It is a white crystalline substance, melting at 218–219° (corr.), and dissolves in dilute alkalies. On heating its alkaline solution, it is changed to the quinazoline, which remains in solution as the alkaline salt and can be precipitated by passing in carbon dioxide.

2,3-*Dimethyl*-5-*nitro*-4-*ketodihydroquinazoline*,



from nitroacetanthranil and methylamine, melts at 203° (corr.). Found: C, 54.43, 54.51; H, 4.08, 4.16; N, 19.24, 19.31. Calculated for $C_{10}H_9O_3N_3$: C, 54.79; H, 4.11; N, 19.17.

2-*Methyl*-3-*ethyl*-5-*nitro*-4-*ketodihydroquinazoline*,

$O_2N.C_6H_3\begin{cases}N=C-CH_3\\CO-N-C_2H_5\end{cases}$, from nitroacetanthranil and ethylamine, melts at 208° (corr.). Nitrogen found, 17.87. Calculated for $C_{11}H_{11}O_3N_3$, 18.00.

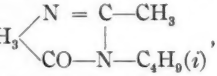
2-*Methyl*-3-*n*-*propyl*-5-*nitro*-4-*ketodihydroquinazoline*,

$O_2N.C_6H_3\begin{cases}N=C-CH_3\\CO-N-C_3H_7(n)\end{cases}$, from nitroacetanthranil and normal propylamine, melts at 204–205° (corr.). Nitrogen found, 16.93. Calculated for $C_{12}H_{13}O_3N_3$, 17.00.

2-*Methyl*-3-*i*-*propyl*-5-*nitro*-4-*ketodihydroquinazoline*,

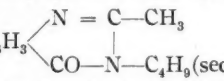
$O_2N.C_6H_3\begin{cases}N=C-CH_3\\CO-N-C_3H_7(i)\end{cases}$, from nitroacetanthranil and isopropylamine, melts at 219–220° (corr.). Nitrogen found, 16.88. Calculated for $C_{12}H_{13}O_3N_3$, 17.00.

2-Methyl-3-i-butyl-5-nitro-4-ketodihydroquinazoline,



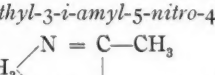
, from nitroacetanthranil and isobutylamine, melts at 202–203° (corr.). Nitrogen found, 16.08. Calculated for $C_{13}H_{15}O_3N_3$, 16.09.

2-Methyl-3-secondary butyl-5-nitro-4-ketodihydroquinazoline,



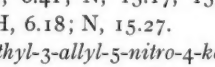
, from nitroacetanthranil and secondary butylamine, melts at 209–210° (corr.) Nitrogen found, 15.84. Calculated for $C_{13}H_{15}O_3N_3$, 16.09.

2-Methyl-3-i-amyl-5-nitro-4-ketodihydroquinazoline,



, from nitroacetanthranil and isoamylamine, melts at 213–214° (corr.). Found: C, 60.82, 60.74; H, 6.12, 6.41; N, 15.17, 15.35. Calculated for $C_{14}H_{17}O_3N_3$: C, 61.09; H, 6.18; N, 15.27.

2-Methyl-3-allyl-5-nitro-4-ketodihydroquinazoline,



, from nitroacetanthranil and allylamine, melts at 160–161° (corr.). It is dimorphous, crystallizing in rhombic plates or long needles. Nitrogen found, 16.95. Calculated for $C_{12}H_{11}O_3N_3$, 17.14.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
June, 1905.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 112.]

SOME EXPERIMENTS ON THE NITRO DERIVATIVES OF FLUORESCEIN.[1]

BY MARSTON TAYLOR BOGERT AND RALPH GARRIGUE WRIGHT.

Received August 3, 1905.

A STUDY of the nitro and amino derivatives of fluorescein has been undertaken, to determine the influence of these groups upon the fluorescence of this well-known substance, both as re-

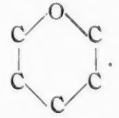
[1] Read at the General Meeting of the American Chemical Society, June 22, 1905. The fluorescein for this investigation was generously supplied by the firm of Kuttroff, Pickhardt & Co., to whom we wish to express our thanks.

gards the number of the groups and their position in the molecule. It is not unlikely, for example, that the influence of the groups present on the phthalic acid nucleus will be found to be quite different from that of similar groups on the resorcinol nuclei.

As the work must now be interrupted for several months, it seems advisable to present the results of our preliminary experiments to date, incomplete as they are. Considerable difficulty was encountered in the reduction of some of the nitro compounds, and much time was consumed in fruitless efforts to isolate these reduction products in sufficient purity to analyze.

Fluorescence is believed to be due to the absorption of light of a certain wave-length and its emission from the absorbing medium as light of a different wave-length. There have been many theories advanced from time to time to account for this phenomenon. Those of R. Meyer[1] and of Hewitt[2] are particularly interesting to organic chemists.

Meyer attributes the fluorescence of organic compounds in solution to the presence in their molecules of a so-called "fluorophore" group. In the fluoresceins, for example, it is the pyrone ring,

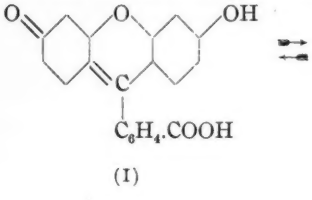


The fluorophore group, however, is not in itself sufficient to cause fluorescence. It must be united with other, generally denser, atomic complexes. Its effect is influenced by substitution, and by the character of the solvent used. The influence of substituting groups in weakening the fluorescence is usually directly proportional to the molecular weight of the substituting group. The nitro group, however, seems to constitute a notable exception, its effect upon the fluorescence being much greater than that of the heavier bromine and iodine atoms. Thus, while the eosins and erythrosins are strongly fluorescent, the entrance of a single nitro group into fluorescein weakens the fluorescence very greatly, while in dinitrofluorescein[3] fluorescence is totally lacking. Rather strangely, however, the so-called "tetranitrofluorescein," although showing no fluorescence in

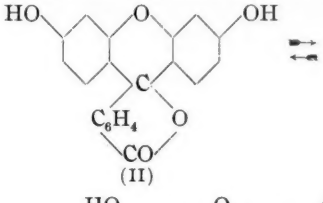
[1] *Z. physik. Chem.*, **24**, 468.
[2] *Ibid.*, **34**, 1.
[3] Baeyer: *Ann. Chem.* (Liebig), **183**, 29.

alkaline solution, gives a strongly fluorescent acetone solution, and the crystalline compound obtained from the acetone solution is colorless, but possesses a distinct yellowish-green fluorescence in the solid state. By the reduction of the nitro fluoresceins, compounds are obtained which give fluorescent solutions again.

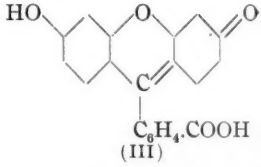
Hewitt[1] ascribes fluorescence to a molecular vibration, which he likens to the oscillation of a pendulum. Thus a fluorescent compound must possess a symmetrical structure of such a character that it may shift freely back and forth from one form to another identical one, through a common intermediate form. In the case of fluorescein, the following would represent such forms:



(I)



(II)



(III)

Substances having the required structure but exhibiting no fluorescence, and substances exhibiting fluorescence without possessing the doubly symmetrical tautomeric structure of fluorescein, are regarded as only apparent exceptions requiring further investigation.

In the present paper, certain nitrofluoresceins are described, together with their behavior on reduction.

Mononitrofluoresceins were prepared from 3- and from 4-nitrophthalic acids and resorcinol. They both dissolve in alkali with a yellowish red color, and weak but distinct green fluorescence. Dinitrofluorescein dissolves in alkalies with a deep blue color and no trace of fluorescence. Attempts to prepare the so-called "tetranitrofluorescein" gave a product which separated from acetone as a white crystalline solid with a distinct yellowish green fluorescence. Analysis of this substance, and of its tetracetyl

[1] *Loc. cit.*

derivative, point to its being a pentanitro derivative, but further proof is necessary to decide this question.

Reduction of the nitrofluoresceins proved a very troublesome and time-consuming task. It was hoped that by suitable modification of well-known reduction processes we could not only obtain direct reduction of the compounds in hand, but might also prepare some of the nitramino bodies. Our results are still very incomplete and unsatisfactory. Some of the products, although crystalline and evidently pure, have not been identified. In other cases, the amino bodies probably in the reduction products could not be isolated.

The aminofluorescein obtained by reducing 4-nitrofluorescein dissolves in alkalies with a green fluorescence. We have not yet been able to isolate the reduction product of 3-nitrofluorescein, or of the supposed pentanitrofluorescein. Diaminofluorescein appears to be a good indicator, giving a bright purple with alkalies and a straw-yellow with acids. Its solutions are fluorescent.

EXPERIMENTAL.

Nitrofluoresceins.

Mononitrofluorescein from 3-Nitrophthalic Acid.—Equal parts by weight of 3-nitrophthalic acid and resorcinol were heated in an oil-bath at 195° until the mass solidified, when it was purified by dissolving in alkaline carbonate and reprecipitating. Crystallized from alcohol, it appeared as a dark brownish red, crystalline solid, melting at 215°. This melting-point agrees with that given for this compound by Reverdin.[1]

It dissolves in alkalies with a yellowish red color, and weak but distinct green fluorescence.

	Calculated for $C_{20}H_{11}O_7N$.	Found.
Nitrogen.....	3.71	3.55

Mononitrofluorescein from 4-Nitrophthalic Acid.—This was prepared in a manner similar to the above, from 4-nitrophthalic acid and resorcinol, and, when pure, forms a crystalline, yellowish brown powder, which sinters and darkens above 300°. It has been patented recently by Kalle & Co.[2]

It gives a yellowish red solution in alkalies, with a weak but distinct green fluorescence.

[1] *Ber.*, **20**, 334 (1887).
[2] D. R. P., 139428 (1903).

	Calculated for $C_{20}H_{11}O_7N$.	Found.
Nitrogen.....	3.71	3.63

So far as we could tell by a superficial examination of these two mononitrofluoresceins, their fluorescence is approximately the same.

Dinitrofluorescein was prepared by the method of Hewitt and Perkin.[1] Crystallized from a mixture of alcohol and carbon disulphide, it forms beautiful red crystals, m. p. 152–153°. On crushing these crystals, an orange-colored powder results. The compound dissolves in alkalies with a deep blue color and no trace of fluorescence, and corresponds with the hydrated body described by Hewitt.

The ammonium salt was also prepared by the action of ammonia gas upon an alcoholic solution of the dinitrofluorescein. It forms red crystals, with a green metallic luster, melting at 243–244°, and agrees in other respects with the properties already recorded for this compound.

(*Tetra-, or*) *Pentanitrofluorescein.*—An attempt was made to prepare tetranitrofluorescein[2] by allowing a sulphuric acid solution of fluorescein to remain for some time in contact with an excess of fuming nitric acid. The solution was then poured into water, the precipitate filtered out, washed, and then boiled with alcohol (to remove any dinitrofluorescein). The residue, crystallized from acetone, formed a white crystalline powder, with a distinct yellowish green fluorescence. It has no definite melting-point, but explodes violently when heated.

The difficulties of the analysis were such that no satisfactory figures could be secured for carbon and hydrogen. The following are the results for nitrogen:

	Calculated for $C_{20}H_5O_{16}N_5$.	Found.		
		I.	II.	III.
Nitrogen.....	12.1	12.3	11.95	11.98

These figures check closely with the theoretical composition of a pentanitrofluorescein.

The compound turns a bright red on standing in the presence of moist air, or on the addition of water. Heating for several hours at 110° does not change this color.

Tetracetyl (*Tetra-, or*) *Pentanitrofluorescein.*—On heating our pentanitrofluorescein with acetic anhydride, it dissolved at first,

[1] *J. Chem. Soc.* (London), **77**, 1324.

[2] Baeyer: *Loc. cit.*

but almost immediately separated again as a fine white crystalline powder, which was recrystallized from acetone. The dried product is fully as, if not more, explosive than the pentanitrofluorescein itself. Its analysis by most of the ordinary methods was abandoned by Hewitt and Perkin[1] as a bad job. We tried a determination by the Kjeldahl method, but with similar lack of success.

However, as the compound is easily saponified, even by hot water, we saponified it with phosphoric acid, and distilled with steam into standardized caustic soda solution. This method gave reasonably satisfactory results. No trace of nitrates or nitrites could be discovered in the distillate, and, as the process was carried out with great care, we believe that we obtained only the acetic acid in our distillate.

	Calculated for		Found.	
	$C_{28}H_{17}O_{20}N_5$.	$C_{28}H_{18}O_{18}N_4$.		
CH_3CO_2H.....	32.3	34.48	32.45	31.18

Considering the difficulties of the analysis, these results agree fairly well, and indicate a tetracetylpentanitrofluorescein. Fuller analytical data are necessary before we can decide whether we are dealing with tetra- or pentanitro derivatives in this and its antecedent compound.

Reduction of the Nitrofluoresceins.

Reduction of 4-Nitrofluorescein.—Four grams of the nitrofluorescein from 4-nitrophthalic acid were dissolved in 40 cc. glacial acetic acid, and treated with 10 grams stannous chloride and 30 cc. concentrated hydrochloric acid. After long standing, a mass of yellowish brown crystals separated, which, on treatment with water, yielded a yellow powder. This powder was purified by repeated solution in alcohol and reprecipitation with water, until it was free from ash. It melts sharply at 281°, and dissolves in alkalies with a green fluorescence. It is probably the aminofluorescein, but the amount of pure substance available was not sufficient for an analysis.

Reduction of 3-Nitrofluorescein.—The reduction was conducted in the same manner as the above. The crude product gave a fluorescent alkaline solution, but the pure amino compound could not be isolated.

[1] *Loc. cit.*

Reduction of Dinitrofluorescein.—Five grams of dinitrofluorescein were dissolved in 35 cc. glacial acetic acid, the solution cooled, and a solution of 12 grams stannous chloride in 40 cc. hydrochloric acid gradually added. Evolution of heat accompanied the reduction, and, after long standing, the solution was filled with a mass of red crystals with a brilliant blue metallic luster. These crystals are apparently the double tin salt of the diaminofluorescein. On treating them with water, a clear solution was obtained only with difficulty and after long stirring. Hardly had the last of the substance dissolved when the solution again became turbid, and in a few minutes was filled with a mass of fine grayish blue needles with brilliant bronze-green luster. Recrystallized from alcohol, these needles changed to plates, of slightly darker color but with the same brilliant luster, melting at 198–199°. In ether or glacial acetic acid, the compound is slightly soluble, and the solutions exhibit a strong greenish fluorescence. In dilute alkalies, the solution appears reddish with violet fluorescence. In strong alkalies, it dissolves with a bright purple color, which changes to a straw-yellow on acidifying. It is apparently a good indicator. In spite of numerous recrystallizations, it was impossible to free the crystals from a trace of some very stubborn impurity, so that the analytical results were uniformly low.

An alcoholic solution of dinitrofluorescein, reduced with stannous chloride and hydrochloric acid gas, gave a brown powder, from which ether extracted a substance forming bright yellow crystals, melting at 249°. Not enough of the pure substance was obtained for analysis.

Reduction of (Tetra-, or) Pentanitrofluorescein.—The pentanitrofluorescein was subjected to the action of various reducing agents—sodium amalgam, magnesium amalgam, aluminum amalgam, tin and hydrochloric acid, stannous chloride, etc. In every instance deep red solutions resulted with no apparent fluorescence in the concentrated state. On diluting, and examining a thin film of the solution, such as is obtained by pouring the liquid slowly down the side of a beaker, the red solution took on a deep and pure blue color, probably due to fluorescence, but no pure reduction product could be separated.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
June, 1905.

II. THE HYDROCARBONS IN LOUISIANA PETROLEUM.

By Charles E. Coates and Alfred Best.

Received August 5, 1905.

This article is a continuation of one published in this Journal, November, 1903. The same methods were employed and the results, taken together, give a fairly complete chemical survey of the various petroleums so far discovered in Louisiana. During the year 1904, three new samples were received. One was from Bayou Bouillon, near St. Martinsville, one was from near Bayou Laroupe on the extreme northeastern limit of the oil territory; one was from near Many, on the extreme western limit. Only the first was received in sufficient quantity for an extended investigation. Of the second, about 200 cc. were sent, this being taken from a prospecting well since abandoned. The third was an oil-bearing sand. The following is the result of the preliminary examination:

	Bayou Bouillon.	Bayou Laroupe.
Specific gravity 25°	0.9669	0.9604
Distillation begins (Engler flask)	275° C.	265° C.
Fraction to 300°, per cent	11	6
Fraction 300°–350°	62	7
H_2S evolved on heating	very little	none
Color of lower fraction	yellow	yellow
Estimated depth of well	900 ft.	400 ft.
Per cent. sulphur in crude oil	0.57	low
Residue	asphaltic	asphaltic
Fuel value, B. T. U.	18500	

The oil sand was extracted with gasoline and the gasoline evaporated, leaving about 40 cc. of black oil as a residue. This, distilled, gave about 10 cc. from 300-350° and about 10 cc. from 350-380°, the residue being asphaltic. Extracted with carbon bisulphide, the sand yielded 5.46 per cent. oil. By drying the sand at 100° for four hours, 0.4 per cent. water was found. In order to compare this oil with one of known properties the following data were obtained:

	Oil sand.	Bayou Bouillon.
Refractive index 25°—fraction 300°–350°.	1.4833	
Refractive index 25°—fraction 350°–380°.	1.5200	
Combining the two fractions:		
Refractive index 300°–380°	1.5013	1.5080
Specific gravity	0.9047	0.9059

The two oils behaved the same towards sulphuric acid and were

similar in physical appearance. These facts taken in conjunction with the above physical constants, would indicate that they are of the same chemical nature. As they represent the extreme eastern and western limits of the Louisiana field, this conclusion is not without interest.

The asphaltic residue obtained had about the same general properties as those described in the previous article. In order, however, to get some data on the technical value of the so-called lubricating fraction, the fraction obtained from the Welsh oil boiling from 300–360° was tested with an Engler viscosimeter, and gave, at 29°, 3.63 as compared with water. Tested with a standard Pennsylvania Railroad pipette at 38°, it gave 2.1 as compared with water. These are about the figures which would be given by the ordinary "mineral" lubricating oils.

The remainder of this article has to do with the nature of the hydrocarbons found in the fraction up to 300°, the so-called illuminating fraction, from Jennings, Welsh, and Bayou Bouillon, that from Breaux Bridge having been discussed already. These fractions were obtained by distilling the crude oil at 760 mm. and collecting the distillate to 300°. Upon redistillation under reduced pressure they all behaved in the same way. It was again found exceedingly difficult to obtain a subfraction of a constant boiling-point, those purified most carefully showing some decomposition even when redistilled at 20 mm. pressure after fuming sulphuric acid ceased to remove anything further. The fractions finally taken for combustion were purified with fuming sulphuric acid, washed with water, then with sodium hydroxide, then with water, dried over calcium chloride and redistilled under diminished pressure. There was much loss by the acid treatment. The subfractions of high boiling-point were dissolved in gasoline before the acid treatment, the gasoline being subsequently removed by distillation. The molecular weights in all cases were determined by the freezing-point method with benzene as a solvent, and the refractive indices with an Abbé refractometer. The distillations were made at different pressures, which was necessitated by the condition of the local water works, these being in process of repair, and owing to the irregularity of the pressure, the figures given for the boiling-points are only approximate.

The Jennings Illuminating-oil Fraction.—Upon treatment as described above, a number of fractions were obtained, of which

three were taken for combustion. The first boiled at 110–115° at 80 mm. Distilled at 760 mm., it boiled at 180–185°. It was water-white and had a marked odor of turpentine, but showed no optical activity in the polariscope. Specific gravity at 22° was 0.8373. Molecular weight found, 150. Calculated for $C_{11}H_{20}$, 152. Combustion gave: Carbon, 86.70; hydrogen, 13.10. Calculated for $C_{11}H_{20}$; Carbon, 86.84; hydrogen, 13.16. Refractive index at 25°, 1.4535. Molecular refraction: Calculated, 48.53; found, 48.76.

The second fraction boiled at 150–155° at 80 mm. It had none of the turpentine odor. Specific gravity at 22° was 0.8649. Molecular weight found was 180. Calculated for $C_{13}H_{24}$, 180. Combustion gave: Carbon, 86.72; hydrogen, 13.41. Calculated for $C_{13}H_{24}$: Carbon, 86.67; hydrogen, 13.33. Refractive index at 25°, 1.4692. Molecular refraction: Calculated, 57.74; found, 57.93.

The third fraction boiled at 200–205° at 80 mm. Specific gravity at 22° was 0.8801. Molecular weight found, 225. Calculated for $C_{16}H_{28}$, 220. Combustion gave: Carbon, 87.59; hydrogen, 12.91. Calculated for $C_{16}H_{28}$: Carbon, 87.27; hydrogen, 12.73. Refractive index at 25°, 1.4805. Molecular refraction: Calculated, 69.44; found, 71.05.

The Welsh Illuminating-oil Fraction.—The first fraction boiled at 145–150° at 80 mm. Specific gravity at 22° was 0.8551. Molecular weight found, 171. Calculated for $C_{12}H_{22}$, 166. Combustion gave: Carbon, 86.57; hydrogen, 13.43. Calculated for $C_{12}H_{22}$: Carbon, 86.74; hydrogen, 13.26. Refractive index at 25°, 1.4662. Molecular refraction: Calculated, 53.13; found, 53.52.

The second fraction boiled at 165–170° at 100 mm. Specific gravity at 25° was 0.8679. Molecular weight found, 186. Calculated for $C_{13}H_{24}$, 180. Combustion gave: Carbon, 86.58; hydrogen, 13.42. Calculated for $C_{13}H_{24}$: Carbon, 86.67; hydrogen, 13.33. Refractive index at 25°, 1.4666. Molecular refraction: Calculated, 57.74; found, 57.45.

The third fraction boiled at 175–180° at 33 mm. Specific gravity at 28°, 0.8736. Molecular weight found, 236. Calculated for $C_{17}H_{32}$, 236. Combustion gave: Carbon, 86.30; hydrogen, 13.44. Calculated for $C_{17}H_{32}$: Carbon, 86.44; hydrogen, 13.56. Refractive index at 25°, 1.4760. Molecular refraction: Calculated, 76.14; found, 76.27.

The Bayou Bouillon Illuminating-oil Fraction.—The first fraction

boiled at 140–145° at 33 mm. Specific gravity at 25°, 0.8557. Molecular weight found, 179. Calculated for $C_{13}H_{24}$, 180. Combustion gave: Carbon, 86.44; hydrogen, 13.17. Calculated for $C_{13}H_{24}$: Carbon, 86.67; hydrogen, 13.33. Refractive index at 25°, 1.4691. Molecular refraction: Calculated, 57.74; found, 58.54.

The second fraction boiled at 170–175° at 33 mm. Specific gravity at 29°, 0.8871. Molecular weight found, 221. Calculated for $C_{16}H_{28}$, 220. Combustion gave: Carbon, 87.00; hydrogen, 12.67. Calculated for $C_{16}H_{28}$: Carbon, 87.27; hydrogen, 12.73. Refractive index at 25°, 1.4828. Molecular refraction: Calculated, 69.44; found, 70.77.

The third fraction boiled at 190–195° at 33 mm. Specific gravity at 27°, 0.8966. Molecular weight found, 235. Calculated for $C_{17}H_{30}$, 234. Combustion gave: Carbon, 87.23; hydrogen, 12.66. Calculated for $C_{17}H_{30}$: Carbon, 87.18; hydrogen, 12.82. Refractive index at 25°, 1.4883. Molecular refraction: Calculated, 74.04; found, 75.16.

The fourth fraction boiled at 200–205° at 33 mm. Specific gravity at 27°, 0.9006. Molecular weight found, 249. Calculated for $C_{18}H_{32}$, 248. Combustion gave: Carbon, 87.30; hydrogen, 12.57. Calculated for $C_{18}H_{32}$: Carbon, 87.1; hydrogen, 12.9. Refractive index at 25°, 1.4916. Molecular refraction: Calculated, 78.64; found, 79.73.

The fifth fraction boiled at 225–230° at 33 mm. Specific gravity at 28°, 0.9104. Molecular weight found, 262. Calculated for $C_{19}H_{34}$, 262. Combustion gave: Carbon, 86.81; hydrogen, 12.55. Calculated for $C_{19}H_{34}$: Carbon, 87.02; hydrogen, 12.98. Refractive index at 25°, 1.4972. Molecular refraction: Calculated, 83.94; found, 84.26.

From an inspection of the foregoing results, it is evident that in the Jennings oil, the series C_nH_{2n-2} and C_nH_{2n-4} are represented, in that from Welsh, the series C_nH_{2n-2} alone was found, while in that from Bayou Bouillon, there were the series C_nH_{2n-2} and C_nH_{2n-4}. Just what the nature of these hydrocarbons is, it is difficult to say, but the existence of the compound $C_{11}H_{20}$ would seem to make it improbable that they are derivatives of dihexahydrodiphenyl as suggested by Mabery and also by Richardson. This question is now under investigation in this laboratory. We have in no case found either optical activity or evidence of an unsaturated compound. We have

obtained the compounds $C_{11}H_{20}$, $C_{10}H_{18}$ and C_8H_{14}, all showing the same properties as the series C_nH_{n-2} referred to above. The results of this work will be published shortly.

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A FULLER STUDY OF THE NEUTRAL SULPHITE METHOD FOR DETERMINING SOME ALDEHYDES AND KETONES IN ESSENTIAL OILS.

BY S. S. SADTLER.

Received August 14, 1905.

PAPERS on this subject have been read at two different times by the author, as follows: October 15, 1903, published in the *Journal of the Franklin Institute*, December 1903, and February 19, 1904.[1] The work was based upon work of Tiemann,[2] Dodge[3] and Heusler,[4] in which neutral sulphites were used to react with the aldehydic constituents of certain essential oils, and the amount of aldehyde present was determined by differences of volume as measured in cassia flasks, etc. Alkali was formed by the reaction, and was indicated by phenolphthalein and, by neutralizing the alkali as formed, the end of the reaction could be ascertained.

The author measured the amount of standard acid required to neutralize the alkali and by calculating the amount, was able to determine the percentage with a fair degree of accuracy. He was in error, however, in judging the extent of the application of the reaction, as in his earlier experiments only citral, cinnamic aldehyde, benzaldehyde, vanillin and formaldehyde were tried, all of which react, although they, as now shown, react differently. These successes were a little misleading.

Burgess,[5] in a paper read December 28, 1903, several months after the reading of the earliest one by the author, but almost coincident with its publication, points out the reactions with citral, cinnamic aldehyde, carvone and pulegone, and states that the same would probably be true of citronellal and olefinic aldehyde.

[1] *J. Soc. Chem. Ind.*, March 31, 1904.
[2] *Ber.*, **31**, 3334.
[3] *Am. Chem. J.*, **12**, 55 (1890).
[4] *Ber.*, **24**, 1805.
[5] *Analyst*, p. 78, 1904.

He does not describe any titration method, however, and refers to measuring in a cassia flask.

His conclusions with regard to the substances that will react are most of them confirmed by the author's coincident or more recent work. He states, however, that carvone reacts with one molecule of sulphite, while the author has abundant experimental evidence to show that it reacts with two molecules and he states that citronellal reacts. The author obtained such feeble results with oil of citronella, that he believes the reaction observed was caused by the small amount of citral contained in this oil, and, furthermore, doubts its activity because of theoretical consideration which will be advanced in this paper. Tiemann[1] only claims that citronella reacts in the presence of sodium bicarbonate.

The substances tried by the author were:

Name.	No. of double bonds.	Class.	No. mols. sulphite.	Remarks.
Citral	2	fatty	2	Reaction slow.
Cinnamic aldehyde	2	aromatic	2	Reaction most energetic.
Benzaldehyde	..	"	1	Reaction moderate.
Vanillin	..	"	1	.....
Carvone	1	ketone	2	Reaction moderate.
Pulegone	1	"	2	"
Formaldehyde	..	fatty	2	Reaction instantaneous.
Citronellal	1	"	..	No reaction.
Camphor	(remote from CHO group) none	.....	..	"
Menthone	"	.....	..	"
Fenchone	"	.....	..	"

The method given by the author[2] has been used for subsequent work. Precautions and observations will be given herewith for the substances studied.

In nearly all cases the flask containing the oil and neutral sulphite was allowed to stand over night to be sure that no more alkali formed. Rosolic acid was used as indicator, and the oils were carefully neutralized with tenth-normal potassium hydroxide before adding the sulphite solution. An important indication of the end of the reaction in most cases is the disappearance of the characteristic odor, noticeable in the cases of cinnamic aldehyde, citral, carvone, pulegone and benzaldehyde. Kerosene was used as a diluent for aldehydes and ketones used by themselves and for oils with high percentages of the same.

[1] *Ber.*, **31**, 3336.
[2] *J. Soc. Chem. Ind.*, March 31, 1904.

CITRAL.

On going over the results with oils containing citral, no additional points of particular interest were found. With lemon oil it was found well to take 15 grams when half-normal hydrochloric acid was used, and heating (immersed in boiling water) was resorted to as soon as the first color that formed with shaking was discharged by the half-normal hydrochloric acid.

The sample of lemon oil was an old one which had previously been found to contain considerably more aldehyde.

Percentage of citral.....	3.69	3.80	3.75
Lemon-grass oil almost 1.5 grams used in 10 cc. of kerosene.			
Percentage of citral.....	72.8	72.2	71.7

CINNAMIC ALDEHYDE.

With oils of cassia and cinnamon the reaction was very much quicker than with citral, especially in the case of the cassia, and in fact some way of rendering it less rapid should be found. The author considered, after getting the material together for this paper, adding the sulphite, to be used, slowly as the sodium hydroxide formed was neutralized so that the alkali could not polymerize or otherwise act upon the aldehyde or its addition product. Heating is only necessary to complete the reaction.

Percentages of cinnamic aldehyde in a sample of nearly pure cinnamic aldehyde.

Cinnamic aldehyde (1.5 grams)...	95.5	94.6	94.6	94.0
Oil of cinnamon (2 grams).....	72.8	72.5	73.8	.....
Oil of cassia (2 grams).....	77.6	78.3	81.5	.....

CARVONE AND PULEGONE.

With compounds containing carvone, such as caraway and dill oils, the reaction is about midway in rapidity between the oils containing cinnamic aldehyde and those containing citral. Heating completes the reaction, after neutralizing several times in the cold.

Carvone (97 per cent.).....	96.4	97.5
Carvone, another sample.....	87.7	89.0
Oil of caraway	52.6	53.6

With pulegone the action is very slow and the reaction is probably 2:1, but this point has not yet been verified by the author. It smelled very strongly of menthol, after the pulegone had been removed by the reaction.

BENZALDEHYDE.

In the case of benzaldehyde it is absolutely necessary to carry out the operation entirely in the cold by violent shaking, and in this case the analyses were carried out by adding the sulphite in small amounts at first. A relatively large amount of rosolic acid or phenolphthalein (as it can be used equally well in the cold) must be used and even then the pink color is very faint, but additions of acid must be kept up until it is completely dissipated. It is especially important to allow the flask to stand over night to see if any additional amount forms.

To further standardize the reaction with benzaldehyde, the clear filtrate was in several cases distilled with steam, and 98 per cent. of the amount taken was recovered. Carbon dioxide was passed through the warm solution to evaporate off the ether.

Steam distillation of the aqueous layers was tried with other substances, but benzaldehyde was the only case where more than a small amount could be recovered. This difference in action may be partly due to the form of combination, but is probably largely due to the different action of steam on the particular aldehydes and ketones themselves.

To standardize the reaction for benzaldehyde, it was thought best to measure the amount of standard alkali (half-normal) used to neutralize the sample and to calculate this to benzaldehyde as the oxidation to acid is so extensive.

Results: 93.5 (not completely decolorized), 96.8, 98.0, 99.0 (fully decolorized).

VANILLIN.

In the case of vanillin there seemed to be a reaction, but the author found difficulty in indicating it. With rosolic acid and phenolphthalein it did not show any formation of alkali, but as pure vanillin dissolved readily in neutral sulphite, it was believed that reaction took place with one molecule of sulphite, as was the case with the benzaldehyde, and the alkali was at once taken up by the vanillin. Previous neutralization of vanillin with alkali, darkened up the solution so that the results were uncertain.

It was found that by taking different amounts of neutral sulphite and vanillin, with more than about one molecule of sulphite to one of vanillin a formation of red color could be observed with a little carefully neutralized cinnamic aldehyde, and with appreciably less that the color did not undergo much change.

A microscopical examination of the residues showed the presence of needle-like crystals of vanillin when in excess at one stage, apparently hygroscopic bunches of very fine crystals of the addition product, with no vanillin at another stage, and then the showing of long effloresced crystals of neutral sulphite itself when more sulphite than the 1 : 1 portion was present.

It is therefore believed by the author that vanillin reacts with one molecule of neutral sulphite.

REAGENTS AND BLANKS.

If the titration is performed hot, it is very hard to decide about the correction to be made for the blank, as the amount of acid necessary to completely discharge the color in the sulphite solution when hot is considerable, but when largely used up in the reaction, would undoubtedly not be so much. The amount of free alkaline reaction in the cold is small and probably even less should be deducted. In this paper, the deductions were about 0.24 cc. of half-normal acid and when 40 cc. were used for titrations; this would not give a large error, if a smaller figure were correct.

The samples of sulphite used by the writer did not vary much, and it is an unexplained fact that the most carefully purified samples showed the stronger alkaline reactions.

NEUTRALIZATION OF SULPHITE SAMPLES.

	Cold. cc.	Hot. cc.
Mallinckrodt sample (anhydrous)	0.24	2.32
General Chemical Co (pure cryst.)	0.22	2.37
General Chemical Co (commercial cryst.)	0.14	1.86
Powers-Weightman-Rosengarten Co. (large, clear crystals)	0.78	2.92

A point to be observed is that correspondingly more of the crystallized salts should be taken as compared with the anhydrous.

THEORETICAL CONSIDERATIONS.

Probably enough substances have now been studied to begin to formulate an opinion as to what influences tend toward combinations of aldehydes and ketones with neutral sulphites.

It may be noticed that double bonds seem to aid in bringing about a reaction when close to the CHO group, as is the case with citral and cinnamic aldehyde.

Proximity of the benzene nucleus to the CHO group as in the case of benzaldehyde and vanillin is probably a factor. It may be

noticed that in the case of the most active aldehyde of high molecular weight, cinnamic aldehyde, both the benzene ring and the double bond are near the CHO group.

Citronellal, $C_{10}H_{18}O$, is like citral, $C_{10}H_{18}O$, except that it lacks two double bonds and the one it has is furthest removed from the CHO group, so if it does not react, as seems to be the case, it would not be anomalous.

With ketones, the only ones the author has found active probably contain double bonds and as near as possible to the CO group. Ketones which probably do not contain any double bonds, such as Japan camphor, menthone and fenchone, do not seem to react.

It might be inferred from the fact that formaldehyde reacts so readily, that the smaller the molecular weight, the more readily the reaction takes place.

The author means to look into the reaction with formaldehyde as the analyses he has made point to two molecules of sulphite reacting, which would mean a rearrangement of the CHO group and not merely saturating double bonds in accordance with Tiemann's reaction. The reactions of benzaldehyde and vanillin, however, seem to indicate that the saturation takes place in the CHO group, as it is unlikely that any of the double bonds of the benzene ring would be saturated, and furthermore there is only one molecule of sulphite entering into the reaction.

Similar to benzaldehyde are salicylic, anisic, cuminic aldehydes and heliotropin which promise well for reacting with one molecule of neutral sulphite.

As Tiemann claimed that citronellal reacted with neutral sulphites in the presence of bicarbonate of soda, a line of investigation with its use should be tried with aldehydes and ketones not reacting with neutral sulphite alone. The author, however, does not see his way clear to do this in the near future.

As heat brought about reaction more rapidly than in the cold, slight pressures were tried with several oils, but it was not found to be useful.

In this paper the author has endeavored to make a few additional analyses of compounds containing citral and cinnamic aldehyde so as to corroborate his previous claim as to the proportions of the reacting substances, to investigate the reaction with benzaldehyde and vanillin, to obtain a satisfactory assay

method for benzaldehyde, and to get further light on the extent of the reactions.

The author regrets that with a very limited amount of time available for this work he has not been able to analyze more samples and obtain more analytical results on those examined, and that, not being directly connected with essential oil interests, he has not had available the fresh samples he would have preferred, and all the varieties he would have liked to examine.

The author wishes, however, to express his thanks to Dr. F. D. Dodge for additional samples, besides those that had been kindly furnished previously.

LABORATORY OF SAMUEL P. SADTLER & SON.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 113.]

THE SYNTHESIS OF 7-NITRO-2-ALKYL-4-KETODIHYDROQUINAZOLINES FROM 4-NITROACETANTHRANILIC ACID, AND FROM 4-NITROACETANTHRANIL.

BY MARSTON TAYLOR BOGERT AND S. H. STEINER.

Received September 14, 1905.

OF THE four possible Bz-nitro-2-methyl-4-ketodihydroquinazolines, three have been described already: the 5-nitro compound by Bogert and Chambers,[1] the 6-nitro by Dehoff[2] and Thieme,[3] and the 8-nitro by Zacharias.[4] In the present paper, the 7-nitro compound is described, thus completing the series.

We have also prepared the 4-nitroacetanthranil, and find that it resembles the 6-nitro isomer[5] in general properties.

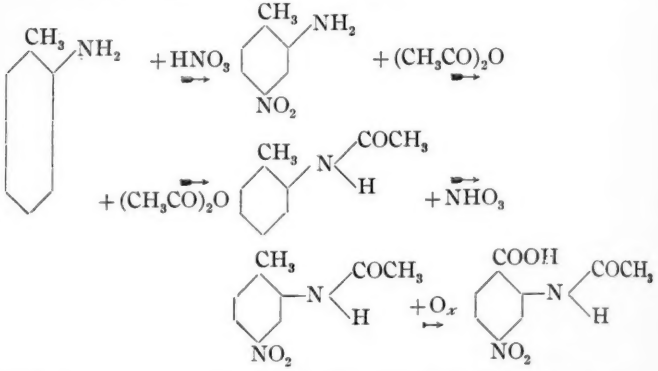
The starting-point for these syntheses was *o*-toluidine. This was converted into 4-nitro-2-acetaminobenzoic acid by two slightly different methods.

I. *o*-Toluidine was nitrated in presence of excess of concentrated sulphuric acid, the 4-nitro-2-toluidine thus produced acetylated, and the acetyl derivative oxidized to the nitroacetaminobenzoic acid.

[1] This Journal, **27**, 655 (1905).
[2] *J. prakt. Chem.* [2], **42**, 347 (1890).
[3] *Ibid.*, **43**, 473 (1891).
[4] *Ibid.*, **43**, 441 (1891).
[5] See Bogert and Chambers: this Journal, **27**, 649; Bogert and Seil: *Ibid.*, **27**, 1305.

II. *o*-Toluidine was acetylated, the acet-*o*-toluide nitrated, and the nitroacettoluide oxidized as before.

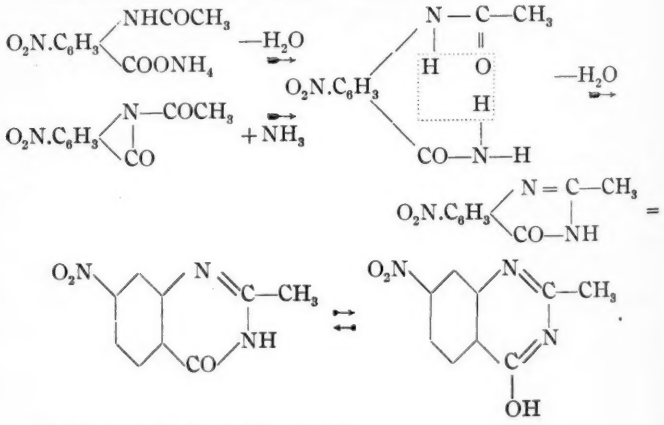
These steps may be expressed as follows:



Of these two methods, the first proved to be much the more satisfactory, both as to yield and purity of product.

The quinazolines were obtained by heating the ammonium salt of the nitroacetanthranilic acid,[1] and by the action of primary amines upon the nitroacetanthranil.[2]

The reactions involved may be outlined thus:



[1] Bischler and Burkart: *Ber.*, **26**, 1349 (1893).

[2] Anschütz, Schmidt and Greiffenberg: *Ber.*, **35**, 3480 (1902); Bogert and Chambers: *Loc. cit.*; Bogert and Seil: *Loc. cit.*

4-Nitro-2-acetaminobenzoic Acid, (4) $O_2N.C_6H_3\begin{cases}COOH\ (1)\\NHCOCH_3\ (2)\end{cases}$.—I. *o*-Toluidine was nitrated in presence of a large excess of concentrated sulphuric acid, by the method of Nölting and Collin,[1] and the product crystallized from alcohol. The 4-nitro-2-toluidine was thus obtained pure (m. p. 107°), and in a yield of 78 per cent. of the theoretical.

The nitrotoluidine was gently boiled for a short time with acetic anhydride, and the product crystallized from alcohol. The nitroacettoluide thus produced melted at 150–151°, as found by Nölting and Collin,[2] and the yield of pure product was 85 per cent. of the theoretical.

II. Acet-*o*-toluide was prepared from *o*-toluidine, by the action of glacial acetic acid, and the product crystallized from water.

This acettoluide was nitrated by the process of Nölting and Collin,[2] as described above, but gave very unsatisfactory results. This method of preparing the nitroacettoluide was, therefore, abandoned in favor of method I.

Oxidation of the nitroacettoluide to nitroacetanthranilic acid was attempted by various methods.

The process of Bedson and King,[3] oxidizing with potassium permanganate in neutral or alkaline solution, gave small yields and impure products. The modification of this process, used by Wheeler and Barnes,[4] by which the oxidation with permanganate is carried out in dilute acetic acid solution, gave a 30 per cent. yield of the desired product.

But the best method by far, proved to be that patented by the Badische Anilin u. Soda Fabrik,[5] in which the oxidation with permanganate is carried out in neutral solution in presence of magnesium sulphate. This gave an 80 per cent. yield of nearly pure nitroacetanthranilic acid.

The crude acid was dried at 70°, added to the least possible amount of boiling alcohol to dissolve it, filtered hot from a small amount of insoluble salts, and allowed to crystallize. The product thus obtained agreed in its properties with the acid described by Wheeler and Barnes.[2] Long boiling with alcohol tends to

[1] *Ber.*, **17**, 263 (1884).
[2] *Loc. cit.*
[3] *J. Chem. Soc.* (London), **37**, 752.
[4] *Am. Chem. J.*, **20**, 219.
[5] D. R. P., No. 94629.

color the product red, apparently from hydrolysis of the acet-amino acid to the free amino acid, since the color could only be removed by recrystallization from acetic anhydride.

4-*Nitroacetanthranil*, (4) $O_2N.C_6H_3\begin{cases}CO\ (1)\\ |\\ N—COCH_3\ (2)\end{cases}$.—

4-Nitroacetanthranilic acid was gently boiled for from five to ten minutes with excess of acetic anhydride, and, on cooling, the anthranil crystallized out in pale greenish cubes, m. p. 137–138° (corr.). It is readily hydrolyzed by moisture, with regeneration of the nitroacetanthranilic acid. With primary amines, it condenses to substituted anthranilamides and quinazolines.

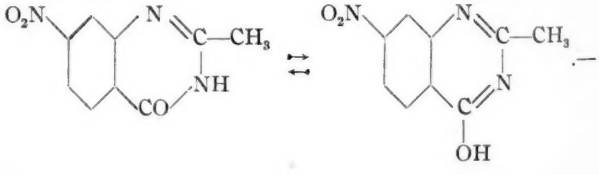
Found: C, 52.09; H, 3.18, 3.11; N, 13.80, 13.81. Calculated for $C_9H_6O_4N_2$: C, 52.39; H, 2.93; N, 13.62.

4-*Nitro-2-acetaminobenzamide*, (4) $O_2N.C_6H_3\begin{cases}CO.NH_2\ (1)\\ NH.COCH_3\ (2)\end{cases}$.—

When 4-nitroacetanthranil is treated with ammonia, some of this amide is apt to be formed, and precipitates. It is freed from any quinazoline by washing with ammonia and then with water, and purified by crystallization from alcohol. It separates from alcohol in small clusters of pale-yellow needles, difficultly soluble in acetic acid, somewhat soluble in ammonia, easily soluble in hot alcohol. When heated quickly, it melts at about 218–223° (corr.), then re-solidifies and does not melt again until the melting-point of the quinazoline (275–277°) is reached. Heated slowly, the loss of water is gradual, and it shows no definite melting-point below that of the quinazoline. Heating with dilute alkali also changes the amide to the quinazoline, and this is the better way of passing from the amide to the quinazoline, since fusion causes considerable decomposition.

Nitrogen found: 18.80, 18.92. Calculated for $C_9H_9O_4N_3$, 18.87.

2-*Methyl-7-nitro-4-ketodihydroquinazoline* (*2-methyl-7-nitro-4-oxyquinazoline*),



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I. *From Ammonium Nitroacetanthranilate.*—The nitroacetanthranilic acid was dissolved in excess of dilute ammonia, the solution evaporated to dryness on the steam-bath, and the residue heated at 225° until the reaction was completed. The cold melt was pulverized, any unchanged ammonium salt extracted with cold water, the insoluble residue dissolved in a little hot, dilute potassium hydroxide solution, and the quinazoline precipitated from the clear alkaline solution by a current of carbon dioxide. Long boiling with the alkali gives a darker colored and less pure product.

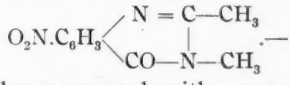
II. *From 4-Nitroacetanthranil and Ammonia.*—The anthranil was warmed with moderately dilute ammonia, and the mixture then acidified with acetic acid. A precipitate resulted consisting of a mixture of amide and quinazoline. By dissolving this precipitate in hot dilute caustic potash, the amide was changed to quinazoline, and by passing carbon dioxide into the alkaline solution the quinazoline precipitated.

The pure quinazoline is difficultly soluble in acetic acid, slightly soluble in hot ethyl acetate, soluble in hot water, in hot alcohol, or in ammonia; easily soluble in alkalies. It crystallizes from alcohol in long pale greenish needles, m. p. 275–277° (corr.).

Found: C, 52.44, 52.48; H, 3.57, 3.58; N, 20.67, 20.74. Calculated for $C_9H_7O_3N_3$: C, 52.64; H, 3.44; N, 20.53.

Hydrochloride, $C_9H_7O_3N_3.HCl$.—The quinazoline was dissolved in the least possible quantity of hot ethyl acetate, the solution filtered, and the filtrate saturated with dry hydrochloric acid gas. The hydrochloride separates in greenish white silky needles, which sinter at about 230°, darken at about 275°, and melt in the neighborhood of 290–295° (uncorr.).

2,3-Dimethyl-7-nitro-4-ketodihydroquinazoline,



4-Nitroacetanthranil was warmed with an aqueous solution of methylamine, the solution filtered hot, and on cooling the quinazoline crystallized out in light yellowish green crystals, melting at 144–145° (corr.); soluble in alcohol.

Nitrogen found: 19.35. Calculated for $C_{10}H_9O_3N_3$, 19.22.

REVIEW OF ANALYTICAL WORK DONE ABROAD IN 1904.

By Benton Dales.

Received September 1, 1905.

A glance at the pages of the *Central-Blatt* will show that one could hardly quote all the titles of analytical papers published last year within the space limit of this review. The effort will be made to treat the reviewed articles generally with sufficient detail that the work may be repeated by an experienced analyst. For the general classification of subjects and for articles in journals, to the originals of which the writer has not access, he acknowledges his indebtedness to the above-mentioned journal.

GENERAL ANALYSIS.

Dittrich (*Ber.*, **37**, 1840) published a scheme for the filtering and igniting of gelatinous precipitates (as ferric or aluminum hydroxide). It consisted in mixing with these, before filtering, a piece of filter-paper shaken to small pieces in water. The mixture will filter easily and give a fine powdery mass on ignition. L'Hote (*Ann. Chim. anal. appl.*, **9**, 305) prepared sulphurous acid for use as a reagent and free from sulphuric by passing sulphur dioxide into a flask nearly full of boiling water, filling it then with boiling water and closing it immediately. Instead of a solution of gaseous hydrogen sulphide in water Sander (*Z. angew. Chem.*, **16**, 202) used a solution of a sulphide, as sodium sulphide, which he decomposed with hydrochloric acid. Windisch (*Wochschr. f. Brauerei*, **21**, 547) examined ten samples of market asbestos for filtering and found that they all contained matter soluble in water, some giving an alkaline reaction.

Optical.—Köthner (*Z. f. Naturw.*, **76**, 81) discussed the problems of spectroscopic analysis for chemistry. The spectroscope is comparatively seldom used as an aid in qualitative analysis, chiefly because of the disturbing influence of spectra produced simultaneously and of complications caused by temperature and pressure. As examples of these influences he stated that a zinc cadmium alloy of nearly equi-molecular composition showed the zinc lines very weakly and a photogram of silver iodide showed no single iodine lines. Other uses of the spectroscope were discussed, as the testing of substances for impurities, the study of molecular processes and the determination of atomic weights. Nasini and Anderlini (*Atti R. Accad. dei Lincei Roma* [5], **13**, I, 368; II, 59) have observed, contrary to the report of Palmieri, that at the temperature of the Bunsen flame helium could not be detected in certain volcanic incrustations from Vesuvius, also that neither the flame nor the electric spark will call forth the helium spectrum from uraninite, monazite, etc. The oxyhydrogen flame does not show the spectrum of hydrogen. In other words under ordinary conditions in flames the characteristic

spectra of the gases are not obtained. They succeeded in obtaining a discontinuous emission spectrum for nitrogen at a much higher temperature, about 3000°. Experiments with iodine above 1000° were not successful, but they thought it was a question only of sufficient temperature. Matthes (*Z. anal. Chem.*, **43**, 73) used the Pulfrich immersion refractometer to determine the purity of many substances and the concentrations of solutions of sodium and potassium halides, acids, grape-sugar, cane-sugar, beer and wine extracts, etc., giving tables for these.

Combustion.—Collie (*J. Chem. Soc.* (London), **85**, 1111; *Proc. Chem. Soc.*, **20**, 174) described a method and the apparatus for the rapid combustion analysis of certain organic compounds. The carbon and hydrogen are determined by burning a known weight of the substance in a known volume of oxygen, the original method having been suggested by Saussure and Prout. The determination depends upon the measurement of gas volumes, hence is accurate; it can be applied only to substances not volatile in a vacuum. The apparatus is complicated, more so than the manipulation. Freiherr von Walther (*Pharm. Centr.-H.*, **45**, 489, 509) modified the filling of the tube for combustion analysis, using copper oxide-platinum asbestos and lead dioxide-silver asbestos for the carbon and hydrogen determination and powdered copper oxide for the nitrogen. He used also a special furnace.

Heating Value.—Alix and Bay (*C. R.*, **139**, 215) pointed out that nearly all coals contain more or less calcium carbonate, which is calculated in these determinations as carbon. The Mahler bomb was said by Arth (*Bull. Soc. Chim.* [3], **31**, 576) to be unsuited to the determination of the heating value of gases which contain only a small proportion of combustible gases. According to him the heating value can be calculated just as accurately and easily from a satisfactory analysis and then it is useless to make the bomb determination. Bazin (*Rev. gen. de Chim.*, **7**, 91) considered the practical steam-making capacity of a combustible material to be two-thirds of its found heating value (calorimetry or combustion). A comparative study of different types of calorimeters was made by Brame and Cowan (*J. Soc. Chem. Ind.*, **22**, 1230) and by Gray and Robertson (*Ibid.*, **23**, 704), and both agreed that reliable results can be obtained only with some form of bomb calorimeter. Gray and Robertson obtained under proper conditions fair results with the William Thompson instrument. Neither of these pairs of workers used the Parr calorimeter, but Mohr (*Wochschr. f. Brauerei*, **21**, 54) did and he decided that it is not yet technically usable. The bomb calorimeter was favored by him also.

Gas.—The separation of methane and hydrogen by fractional combustion caused by heated palladium wire was said by Richardt (*J. f. Gasbel.*, **47**, 566, 590) to work all right under proper conditions. The wire must not glow and the contact of gas with

the wire must be neither too long nor too short. Ethane behaves like methane with regard to hydrogen, but it cannot be separated from methane by this means. Neither can ethylene. Macri (*L'Industria chimica*, **6**, 285) stated that the Clemens Winkler method of fractional combustion over palladium asbestos for the separation of hydrogen and methane is not satisfactory for separation, but may be used for the determination of both together. Morelli and Colonna (*L'Industria chimica*, **6**, 61) have modified the Orsat-Lunge apparatus so as to work with small amounts of gas in the presence of mercury, and to be able to carry out the combustion of explosive mixtures without danger. Sodeau (*Chem. News*, **89**, 61) also modified the Orsat apparatus, putting in place of the cuprous chloride pipette a Winkler combustion pipette to which is attached its own level bottle. The carbon monoxide and hydrogen are then determined by combustion. St. Martin (*C. R.*, **139**, 46) determined carbon monoxide in the air by shaking thirty minutes with fresh dog's blood so diluted as to contain about 0.15 per cent. of haemoglobin, and examining spectro-photometrically and reading off the content of carbon monoxide in air from tables. Wohl (*Ber.*, **37**, 433) has extended his method of gas analysis by measurement of pressures to the determination of heavy hydrocarbons and to combustion analysis. In another article (*Ibid.*, **37**, 429) he pointed out an error in the calculation of results of combustion analyses of gases. Avogadro's rule must be considered to hold good for the relations between hydrogen, oxygen, carbon monoxide and methane for the errors do not exceed 0.2 per cent. But with carbon dioxide this is not so; the difference in molecular volume compared to carbon monoxide is 0.6 per cent. and to methane 0.8 per cent. Besides the main contraction demanded by Avogadro's rule there is in burning carbon monoxide a further contraction of 0.6 per cent. of the carbon dioxide volume present, so that in calculating carbon monoxide one would find 1.2 per cent. too much. His formulae for the calculation of hydrogen, carbon monoxide and methane are: $H = K - O - 0.006\ CO_2$; $CO = {}^1/_3K - O + {}^3/_4CO_2 + 0.006\ CO_2$; $CH_4 = -{}^1/_3\ K + O - {}^1/_3CO_2$ (K = contraction, O = oxygen used and CO_2 = carbon dioxide formed).

Soil and Fodder.—Edwards (*Chem. News*, **89**, 183) described a rapid method for the analysis of soils, intended chiefly for analytical chemists at manure works. The determinations include water, organic matter, phosphoric acid, iron oxide and alumina, lime, potash and nitrogen. Hall (*Proc. Chem. Soc.*, (London) **20**, 152; *J. Chem. Soc.*, **85**, 950) discussed the mechanical analysis of soils by the Osborne settling method with and without previous treatment with dilute acid and ammonia. His results show that it is better to treat with acid and ammonia before subjecting the material to the fractional settling. Hazard (*Chem. Ztg.*, **28**, 210)

gave a shortened method for the determination of potash in soils, potash residues, etc. He evaporated the acid soil solution in a porcelain dish, extracted the residue with water in platinum, precipitated with ammonia and ammonium carbonate, heated the precipitate to dryness and ignited to drive off the ammonium salts and burn up organic matter. He then extracted the residue with hot water and determined potassium in the filtrate with chlorplatinic or perchloric acid. A method for the volumetric determination of the humus content of the soil by means of permanganate solution was proposed by Istscherekow (*J. f. exp. Landw.*, **5**, 55). He boiled the crushed soil for forty or fifty minutes with permanganate solution, and titrated the excess with oxalic acid, or to dissolve the dioxide formed, added excess of oxalic acid and titrated with permanganate.

Duschetschkin (*J. russ. phys.-chem. Ges.*, **36**, 71) prepared crude fiber from fiber containing vegetable lignin by heating for from one and one-half to six hours (according to lignin content) with two parts of sodium peroxide and six parts of magnesium sulphate to one part of substance, with preliminary treatment of substance with 1 per cent. sodium hydroxide solution if lignin content be large. Lührs (*Chem. Ztg.*, **28**, 357) determined the sand content of a commercial fodder by heating it in a Kjeldahl apparatus for about half an hour with concentrated sulphuric acid, adding an oxidizing agent till the solution cleared, cooling, diluting with water, decanting from the sand, washing and weighing this in platinum. Mayer (*Chem. Ztg.*, **28**, 406) considered Lührs' method too involved and extracted the fodder with chloroform in a short-tubed separatory funnel, then allowed the sand settlings to run into a platinum dish and ignited.

Water.—Drawe, Procter, Auerbach and Basch (*Chem. Ztg.*, **27**, 1219, 1277; **28**, 16, 31) had each a different explanation for the occasional residual alkalinity of a hard water after long boiling. Pfeifer had ascribed this alkalinity to magnesium carbonate which is not insoluble in water. Drawe claimed a soda content for every natural water, which Procter said could not be as long as the water showed a permanent hardness. Procter apparently favored Pfeifer's explanation. Auerbach maintained that the small amounts of carbonate in solution are completely dissociated any way, so that it makes no difference whether one considers the alkalinity due to sodium carbonate or to calcium or magnesium carbonate; he favored soda. Basch stated that soda in solution is to be regarded as sodium hydroxide and primary sodium carbonate; he said Pfeifer's statement that soda reacts not at all or only very slightly with phenolphthalein is not true. Soltsien (*Pharm. Ztg.*, **49**, 218) added to this argument that the evaporation residues of waters ordinarily react alkaline, often strongly so, and that this is due in most cases to magnesium carbonate because sodium carbonate is found in ordinary waters, if at all, only in

traces. Legler (*Pharm. Centr.-H.*, **45**, 585) gave a new method for the determination of the degree of hardness of a water. He evaporated the water sample to dryness with excess of hydrochloric acid, or if it was hard, boiled it with excess of tenth-normal hydrochloric acid till all the carbon dioxide was gone, and then neutralized with tenth-normal alkali in presence of aqueous methyl orange. The neutral water, or water residue dissolved in water, was then treated with an excess of a definite mixture of potassium oxalate and sodium hydroxide, boiled, made up to a definite volume, and one part of the clear filtrate used for the determination of calcium, the other for magnesium. For this purpose one part of the filtrate was treated with excess of tenth-normal sulphuric or hydrochloric acids and neutralized in presence of rosolic acid or of phenolphthalein, while the other portion was acidified, warmed and titrated with permanganate. Buttenberg (*Gesundh.-Ing.*, **26**, No. 15) found that distilled water would attack lead strongly. Lenormand (*Bull. Soc. Chim.* [3], **31**, 139) showed that a salt or sweet water solution will take up organic matter from filter-paper so that it is inadvisable to filter waters before analysis. Lohmann (*Z. öffentl. Chem.*, **9**, 458) distinguished between distilled and ordinary water in artificial mineral waters by their optical behavior; a layer 50–75 cm. thick will appear greenish blue if distilled water is used, whereas it will appear brownish with ordinary water. The silica test recommended by Silber the author stated to be of no value, because silica ought to be added to give the water a mineral-like taste.

Electroanalysis.—Brochet and Petit (*C. R.*, **138**, 359, 419) gave some experiments with different metals and different electrolytes using the alternating current, and opposed LeBlanc's view that the solution of copper in potassium cyanide solution is caused by the formation of complex ions under the influence of the current. There are three classes of cases where no formation of complex ions takes place, according to these authors. They are (1) stable electrolytes (with evolution of oxyhydrogen gas), (2) solution of the electrodes, and (3) oxidation or reduction. Examples were given. Pearce and Couchet (*Ibid.*, **138**, 361) observed that reduction of higher stages of oxidation by means of the alternating current depends upon the nature of the electrodes as well as upon current density and number of alternations. With small current density only solution of the electrodes is observed. The reduction of ferric alum is slight with platinum, greater with aluminum, lead or cadmium, and nearly quantitative with iron electrodes. Haber and Schwenke (*Z. Elektrochem*, **10**, 143) devised an electrochemical method for determining the amount of attack on glass, especially bottle-glass, by water. Water which would conduct was placed in the bottles and then they were heated for five hours at 80°. Electrodes were introduced through the neck and the conductivity measured every

hour. The current strength corresponding to 30, 20 and 10 volts tension was determined with an ammeter and the resistance calculated graphically. The conductivity of the water minus the initial conductivity divided by the time of action gives for every glass its rapidity of solution, a value nearly constant for each glass, and characteristic. Some of the brown and green wine-bottles were nearly as little attacked as Jena glass.

Volumetric.—Kühling (*Chem. Ztg.*, **28**, 596, 612) and Lunge (*Ibid.*, **28**, 701) had a portion of their discussion over the suitability of potassium tetroxalate as a standard titration substance. The discussion was begun in 1903, Kühling maintaining that the tetroxalate prepared according to his directions was satisfactory, while Lunge insisted that it would not yield as good results as would soda or Sorenson's sodium oxalate. Raschig (*Z. angew. Chem.*, **17**, 577) recommended as original titration substances crystallized oxalic acid and sodium carbonate, also a water solution of gaseous hydrochloric acid, and further sulphur dioxide solution for iodometric titrations. Raschig's method of standardizing the gaseous hydrochloric acid solution was described by Moody in 1898, according to Lunge (*Ibid.*, **17**, 886). Lehfeldt (*Pharm. Ztg.*, **49**, 146) recommended potassium biiodate for iodometry, sublimed oxalic acid (Merck) for acidimetry, and the preparation of hundredth-normal solutions of hydrochloric acid and caustic potash by titration against oxalic acid in the presence of iodeosin. Cantoni and Basadonna (*Ann. Chim. anal. appl.*, **9**, 365) criticized the ordinary methods of standardization of permanganate with iron wire, Mohr's salt and oxalic acid, and recommended the iodometric method of Volhard. Dupré (*Z. angew. Chem.*, **17**, 815) likewise recommended the Volhard method, preferring it to the electrolytic because of its simplicity. Skrabal (*Z. anal. Chem.*, **42**, 741) had the end of his argument with Classen regarding "Classen electrolytic iron." Skrabal maintained that it was impure. In another article (*Ibid.*, **43**, 97) he gave a couple of methods for preparing ferrous ammonium sulphate from which he obtained iron by the Classen method, but after it was precipitated it was carried by means of a weak current from one electrode to the other. Gardner and North (*J. Soc. Chem. Ind.*, **23**, 599) found that pure permanganate in pure water would preserve its original strength for at least twelve months. Ammonium oxalate deteriorated at the rate of about 1 per cent. a fortnight for seven months. Potassium bromide was recommended by Berti (*Bull. de l'Assoc. d. Chim. de Sucr. et Dist.*, **21**, 1234) and sodium sulphide by Beulaygue (*C. R.*, **138**, 51) as indicators for the determination of sugars by means of Fehling's solution. A violet color, due to the formation of water-free cuprous (?) bromide, indicates that there is still copper in solution when a very small amount of solution is brought into contact with a small crystal of potassium bromide on porcelain and then

concentrated sulphuric acid added. A yellow color, due to free bromine, is obtained when the copper is all out of solution. If a double layer of filter-paper be touched with the Fehling's solution and the untouched one of the two paper layers then touched in the moistened spot with freshly prepared 10 per cent. sodium sulphide solution, the paper will show dark by transmitted light at the touched spot as long as copper is present in solution. Robin (*Ann. Chim. anal. appl.*, **9**, 130; *C. R.*, **138**, 1046) prepared a new indicator by heating the yellow mimosa blossoms in 200 cc. of water to beginning boiling and after cooling adding 50 cc. of neutral 95 per cent. alcohol, allowing to settle and filtering into a brown bottle. It gives an intensely yellow color with alkalies and is colorless in acid solutions. On evaporation of some of the indicator with material containing boric acid, the residue is yellow and becomes red with a few drops of soda solution. Without boric acid the indicator residue would be gray and yellow under these two conditions. Scholtz (*Z. f. Elektrochem.*, **10**, 549) determined the strength of indicators as bases or acids by titrating an acid solution with a base, like caustic potash, when the stronger acid indicator will change color first (as *p*-nitrophenol before phenolphthalein). If basic indicators are mixed with the acid the order in which they change color in the above titration is weakest base, strongest base, strongest acid, weakest acid. The following is the order found by the author, beginning with the strongest acid: (1) alizarinsulphonic acid, iodeosin; (2) *p*-nitrophenol; (3) luteol; (4) haematoxylin, rosolic acid; (5) litmus; (6) turmeric; (7) phenolphthalein. Of those with less sharp color changes, cochineal is stronger than litmus, alizarin lies between *p*-nitrophenol and litmus, and fluorescein between iodeosin and litmus. Cyanine is a stronger basic indicator than methyl orange or the tropaeolins. Rosenthaler (*Arch. der Pharm.*, **241**, 589) described the spontaneous change which takes place in Fehling's solution.

Microchemical.—Behrens (*Z. anal. Chem.*, **43**, 333) gave a goodly number of microchemical reactions for the detection of different classes of organic bases as the anilines, aminophenols, benzylamines, diamines, pyridines, various alkaloids, etc. Paraffin oil was recommended by Harz (*Z. f. wiss. Mikrosk.*, **20**, 179; **21**, 25) as a substitute for Canada balsam for permanent microscopical preparations, and a solution of 1 part of iodine in 100 parts of gently warmed paraffin oil as an imbedding medium. Wieler (*Chem. Ztg.*, **28**, 1014) pointed out a structure resembling cell structure in basic precipitates, especially basic copper carbonate, and said that such structure might be looked for in natural precipitates such as minerals, and succeeded in showing a honeycomb-like structure in malachite, dolomite and carbonate of nickel.

ANALYSIS OF ORGANIC COMPOUNDS.

Gasparini (*Atti R. Accad. dei Lincei Roma* [5], **13**, II, 94) gave a

new method for the destruction of organic matter in toxicological analysis. He electrolyzed the nitric acid solution, using a current of 4 to 6 amperes and 8 volts. The oxidation was sometimes complete in a few hours and sometimes required days. Some metals (copper, lead, silver, etc.) colored the solutions near the electrodes or gave precipitates. Tin and antimony were precipitated as higher oxides, while arsenic remained in solution as arsenic acid. Monthulé (*Ann. Chim. anal. appl.*, **9**, 308) destroyed organic matter for the determination of phosphorus and arsenic as follows: he saturated the substance in a porcelain crucible with a solution of magnesium oxide in nitric acid (sp. gr. 1.38) of which 100 cc. contained 10 grams of magnesia. This mixture he evaporated as far as possible on the water-bath, then on a sand-bath and finally ignited over a free flame at low redness. If a carbonaceous residue remained, he added nitric acid, dried and ignited again. He then dissolved the residue and treated the solution with magnesia mixture. Von Konek (*Z. angew. Chem.*, **17**, 771, 886, 888, and 1093 (with Zöhls)) described the use of sodium peroxide in organic analysis, both qualitative and quantitative. By its use all the ordinary elements except hydrogen and oxygen may be detected. The author used a thick-walled nickel or steel cylindrical crucible of about 2 cm. diameter and provided with a screw cover which had a hole in the middle, and into which a nickel or steel tube 10 cm. long and 1 to 2 mm. inside diameter fitted. Five to 10 grams of dry sodium peroxide were placed in the crucible, a good knife point full of the substance added, the mixture stirred, the cover screwed on, the crucible placed in a dish of cold water and the hot wire for ignition thrown in through the metal tube. The combustion is explosive. Carbon is oxidized to carbon dioxide, nitrogen and phosphorus to the pentoxides, the halogens to the halides, sulphur to sulphur trioxide, and arsenic, selenium, tellurium, boron and antimony to arsenic, selenic, telluric, boric and antimonic acids, the heavy metals remaining as oxides or hydroxides. Some quantitative methods, especially an indirect one for carbon, were given. Von Konek criticized also the form of crucible recommended for a similar use by Pringsheim, who replied to this (*Ibid.*, **17**, 1454). Pringsheim (*Ber.*, **37**, 2155) also published an article along lines similar to the above. Herzog (*Z. f. Farben- und Textilchemie*, **3**, 259) showed that natural and artificial silk may be distinguished from each other by their behavior toward polarized light; artificial silk shows dichroism, natural does not.

Alcohols and Acids.—Gnehm and Kaufler (*Z. angew. Chem.*, **17**, 673) proposed a new method for the determination of methyl alcohol in formaldehyde. The latter compound forms a condensation product with sodium sulphanilate, and the methyl alcohol may then be driven off by distillation. They determined the alcohol from the density of the distillate, but Bamberger (*Ibid.*, **17**, 1246) said that the old method of distilling the alcohol

after condensation with primary sodium sulphite gives better results. Kling and Viard (*C. R.*, **138**, 1172; *Bull. Soc. Chim.*, (3), **31**, 783) gave a method for distinguishing the primary, secondary and tertiary alcohols of the fatty series. Tertiary alcohols decompose into unsaturated hydrocarbons at or below the boiling-point of naphthalene, secondary alcohols do not decompose before the boiling-point of anthracene is reached, while primary ones remain undecomposed at this temperature. Then a V. Meyer vapor-density determination first in naphthalene vapor, then in anthracene vapor, will show whether the alcohol is a primary, secondary or tertiary one. Ley (*Pharm. Ztg.*, **49**, 149) proposed the following method for the determination of tartaric acid. He heated the water or alcohol solution of tartaric acid, treated it with alcoholic zinc acetate solution, heated again, then added 100–150 cc. of alcohol and 5 cc. of 50 per cent. acetic acid. The whole was then heated on the water-bath, filtered by suction, washed and ignited. Dubosc (*Ann. Chim. anal. appl.*, **9**, 45) proposed to determine sulphocyanates in the presence of salts which give precipitates with silver nitrate by oxidizing the sulphur of the sulphocyanate to sulphate. He used the chlorine liquor (18–20 grams of active chlorine per liter) obtained from the electrolysis of chlorides for this oxidation. In 50 cc. of water he took enough of the sulphocyanate to yield probably 0.2 to 0.4 gram of barium sulphate, added to the solution 2 grams of barium chloride dissolved in 50 cc. of water and then gradually 50 cc. of the electrolytic liquid. This was allowed to stand some ten minutes, was then acidified with hydrochloric acid, boiled and filtered. A method for the volumetric determination of hydrocyanic acid in cyanides was given by McDowall (*Chem. News*, **89**, 229). He used an ammoniacal copper sulphate solution. The passage to colorless is sharp and the presence of chlorine is without influence.

Carbohydrates.—Benz (*Z. f. Unters. Nahr.-Genussm.*, **7**, 84) suggested that the hour digestion or half-hour shaking of the accepted method for the determination of soluble carbohydrates in food material be changed to twenty-four-hour digestion, because in one hour not all of the actually soluble carbohydrates go into solution. Goodwin and Tollens (*Ber.*, **37**, 315) dried furfurolphloroglucide at 103° in a current of hydrogen to avoid oxidation and found that its formula is $C_{11}H_8O_4$, not $C_{11}H_6O_3$. Two new methods of sugar determination were proposed by Oerum (*Z. anal. Chem.*, **43**, 356). In one the cuprous oxide precipitated as usual was separated from the liquid by means of an asbestos filter, dissolved in nitric acid and the copper determined by the use of Meisling's universal colorimeter. The other was a modification of the Sachsse mercury method. A solution of 18 grams of pure dry mercuric iodide, 25 grams of potassium iodide and 80 grams of caustic potash was made and diluted to one liter with water. Of this solution 20 cc. were

boiled in a small flask with 80 cc. of water, then 5 cc. of urine so diluted as to contain not more than 1.3 per cent. of sugar were added and the boiling continued for a few minutes. The precipitated mercury was filtered through a good filter, washed with hot 1 per cent. hydrochloric acid, then with water and dissolved in nitric acid. The solution was diluted and the mercury determined by the Volhard method, using ammonium ferric alum for indicator. Another sugar determination was given by Rosenthaler (*Z. anal. Chem.*, **43**, 252). When sugars are oxidized by alkaline copper solution acids are formed and these neutralize a portion of the alkali in the solution. If a portion of the alkaline copper solution alone be titrated with normal acid and then a similar portion after the sugar treatment, the difference between the two figures will give the amount of alkali neutralized by the acids from the sugar. In practice Rosenthaler added excess of normal acid and titrated back with normal alkali, using phenolphthalein for indicator. Riegler (*Bull. Soc. des Sciences de Bucarest*, **13**, 20) gave a rapid gasometric method for the determination of sugar in urine. The sugar was oxidized by boiling the diluted liquid with a little potassium permanganate, adding the liquid to more permanganate, cooling, evolving by means of sulphuric acid and measuring the carbon dioxide from the carbonate formed. $C_6H_{12}O_6 + 8KMnO_4 = 4K_2CO_3 + 2CO_2 + 8MnO_2 + 6H_2O$. Pflüger (*Pflüger's Arch.*, **103**, 169) gave a shortened method of determining glycogen. He heated 100 grams of fresh material for two hours in 100 cc. of 60 per cent. potassium hydroxide. On cooling, 200 cc. of water were added and 400 cc. of 96 per cent. alcohol. After filtration the precipitate was washed once with a mixture of one volume of 15 per cent. caustic potash and two of 96 per cent. alcohol, then with 66 per cent. alcohol and finally dissolved in boiling water. He neutralized the solution, removed the albumen precipitated, neutralized again and then added hydrochloric acid to a concentration of 2.2 per cent. The inversion required three hours. The solution was then cooled, neutralized, filtered and the sugar determined. The sugar value was multiplied by 0.927 for the glycogen value. Cellulose may be determined in food products, etc., by a modification of this Pflüger glycogen method, according to Simon and Lohrisch (*Z. physiol. Chem.*, **42**, 55). They heated 10 grams of the substance for one hour on the water-bath with 50 per cent. caustic potash, and on cooling added 3 to 4 cc. of hydrogen peroxide. The material all dissolved, at least if treatment with peroxide were repeated. On addition of one-half volume of 96 per cent. alcohol the cellulose was precipitated. It was filtered by suction on to a hardened filter, washed with water and weighed.

Alkaloids.—Kley (*Z. anal. Chem.*, **43**, 160) found that the alkaloids might be very well distinguished by measuring roughly their indices of refraction. Small crystals were placed in a series of solutions of varying but known indices of refraction, placed

between two nicols, and the comparison carried on till the index of the crystal and of the liquid were the same. Among the large number of analytical articles dealing with the characteristics of alkaloids, attention will be called here only to two by Leger (*J. Pharm. Chim.* (6), **19**, 329, 479) and to nine by Reichard (*Chem. Ztg.*, **28**, 299, 339, 912, 977, 1048, 1102; *Pharm. Ztg.*, **49**, 523, 855; *Pharm. Centr.-H.*, **45**, 645). Leger gave the results of investigations upon the root bark of the pomegranate, upon coca, belladonna, nux vomica, *fabae ignatii*, ipecac and Peruvian bark. Reichard's investigations covered the reactions of morphine, cocaine, atropine, strychnine, brucine and antipyrine. Wörner (*Pharm. Ztg.*, **49**, 628) stated that Reichard's new test for morphine with formaldoxime and sulphuric acid is practically the known Marquis test with formaldehyde and sulphuric acid.

Coloring Materials and Tannins.—Lambrecht and Weil (*Ber.*, **37**, 303) gave a quick method for distinguishing between rosaniline and pararosaniline. The former dissolves completely in twenty volumes of 30 per cent. hydrochloric acid on warming and yields no precipitate when this solution stands, while pararosaniline forms with the same amount of acid difficultly soluble hydrochlorides which crystallize out on cooling nearly completely. The addition of 0.5 per cent. of pararosaniline can be detected on twelve hours' standing by the brown crystals. Riegler (*Z. anal. Chem.*, **43**, 539) used an alkaline alcoholic hydrazine solution as a test for blood. His reagent he prepared by dissolving 10 grams of sodium hydroxide in 100 cc. of water, adding 5 grams of hydrazine sulphate, 100 cc. of 96–97 per cent. alcohol, and filtering after two hours. Blood shaken with this solution and allowed to stand gives a magnificent purple-red solution of haemochromogen. Shaken vigorously in the air the solution turns greenish and shows the absorption spectrum of haematin (one band). On standing, the solution turns red again, showing then the absorption of haemochromogen (two bands, similar to those of the original blood solution, but moved a little toward the violet). Parker and Payne (*J. Soc. Chem. Ind.*, **23**, 648) proposed a new method for the determination of tannins which rests on the fact that digallic acid forms, with excess of lime, a basic salt insoluble in water. $C_{14}H_{10}O_9 + 4Ca(OH)_2 = C_{14}H_{10}O_9Ca_4(OH)_8$. Bogh (*Collegium*, 1904, p. 301) called attention to the fact that the equivalent used by Parker and Payne (40 liters of fifth-normal calcium hydroxide to 322 grams of tannin) is all right for the tannins of the pyrogallol series, but that for the catechol series it must be multiplied by $^3/_2$. With old tannin material the method gives results which do not agree with those obtained by the gravimetric method. Dreaper (*Chem. News*, **90**, 111), in view of the above-mentioned method, called attention to his own method of precipitation by means of calcium or barium salts and subsequent titration with copper sulphate, published in 1893.

Parker and Payne said that their method gives results agreeing with those of the common method, but Dreaper showed in 1893 that the latter would give values for tannic acid in a substance certainly free from it, and hence was analytically worthless. Dufour (*Collegium*, 1904, p. 337. Extract from *La Conceria*) showed that the caramel obtained from starch, sugar, etc., which gives none of the reactions characteristic of tannin, is more or less completely absorbed with the tannin in the official analysis. Wislicenus (*Z. angew. Chem.*, **17**, 801) found that aluminum hydroxide may be used as the precipitating agent for the tannins instead of powdered hide.

Ethereal Oils and Wine.—Fendler (*Ber. d. pharm. Ges.*, **14**, 208) gave a method of determining water, insoluble matter, pure rubber and resin in crude rubber practically in one operation. The water was determined by simply drying over sulphuric acid. The insoluble impurities were obtained by treating 2 grams of the finely divided sample in a 100 cc. measuring flask with petroleum ether till nothing more would go into solution, then adding petroleum ether to 100 cc. and allowing to settle. The mixture was then filtered through a layer of glass wool in an Allihn tube, 50 cc. into a 50 cc. flask, the rest into another vessel. The residue on the glass wool, washed with the solvent, dried and weighed, gave the insoluble impurities in 2 grams of crude rubber. The pure rubber in 1 gram of crude was determined in the first filtered 50 cc. by shaking with about 70 cc. of absolute alcohol in a weighed 200 cc. flask, pouring off the petroleum ether-alcohol mixture, washing the usually balled mass of pure rubber with alcohol, drying in a water-drying oven with a blast of air and weighing flask and contents. The resin in 1 gram of the crude rubber was determined by distilling the petroleum ether-alcohol mixture and the alcohol washings mentioned above from a weighed flask, and drying and weighing the residue. In another article (*Ibid.*, p. 215) Fendler compared three of the newer methods for rubber analysis. They were that of Harries (*Ber.*, **34**, 2991; **35**, 3256, 4429; **36**, 1937), of Weber (*Ibid.*, **35**, 1947; **36**, 3103) and his own just described. He found that the methods of Harries and Weber gave like results for pure rubber in crude, and that both were in many cases too high; that Harries' method was preferable to Weber's because of its greater simplicity; that the values for insoluble constituents obtained by either method were wide of the mark, and that his own method gave usable results in the analysis of crude rubber and was of value because of its simplicity. Raikow and Schtarbanow (*Chem. Ztg.*, **28**, 886) observed that it was possible to obtain a measure of the volatile constituents besides alcohol in wine by comparing the alcohol content found by determination of the flashing-point of the wine (which result is always too high) and by distillation. Spica (*Gaz. chim. ital.*, **33**, II, 482) detected salicylic acid in wine by converting it into

picric acid and coloring wool yellow with it. If the yellow color were not due to picric acid or to salicylic acid, it would not color wool a second time, if the color were removed by alkali, the liquid made acid and fresh wool dipped in it. The first coloration would be proof of salicylic acid, if the original extraction were made with carbon disulphide instead of ether.

Milk, Blood and Fats.—Ertel (*Milch-Ztg.*, **33**, 81) took exception to some of the statements of Ripper concerning milk. Ripper stated that the index of refraction of the milk serum was a criterion as to whether the milk came from a sound or a sick cow, the normal being 1.3430-1.3442 while that of milk serum from sick cows is 1.3410-1.3427. Ertel showed that this index of refraction for the milk of sound cows does not vary much and yet often exceeds the limits given by Ripper, going more often above than below, and also that that of sick cows' milk often runs above 1.3440. It varies more with sick than with well animals and will vary with the same animal. Salaskin and Pupkin (*Z. physiol. Chem.*, **42**, 195) used the Salkowski principle (titration of the ammonia driven out of ammonium salts by blood) to determine the alkalinity of blood, but Folin (*Ibid.*, **43**, 18) stated that ammonia added to blood can not be completely driven out at any temperature. Toward the end of 1903 Partheil and Ferié (*Arch. der Pharm.*, **241**, 545) published a separation of the saturated fatty acids depending in large measure upon the solubilities of the lithium salts, and they obtained some very good results. But Farnsteiner (*Z. f. Unters. Nahr.-Genussm.*, **8**, 129) and Fahrion (*Z. angew. Chem.*, **17**, 1482) both unconditionally condemned the method. Heermann (*Chem. Ztg.*, **28**, 53, 60, 702) criticized most of the usual methods for the determination of small amounts of sodium carbonate and hydroxide in soaps and gave an improvement on his modification of the salting-out method. The first two articles were the signal for a polemic with Schmatolla (*Ibid.*, **212**, 611, 711), in which Berg (*Ibid.*, **212**, 691) joined, upon the alkalinity and the dissociation of soaps. Heermann determined the sodium hydroxide by precipitating the fatty and carbonic acids with barium chloride, then titrating the liquid with standard acid, using phenolphthalein as indicator. For the sodium carbonate, he salted out with sodium chloride and titrated directly with methyl orange as indicator, and then subtracted the value found for sodium hydroxide; or he dissolved the soap in absolute alcohol, saturated the sodium hydroxide with carbon dioxide, filtered, washed with cold absolute alcohol, dissolved the precipitate in hot water and titrated with methyl orange as indicator. Schmatolla stated that soaps can split in two ways and endeavored to show why Heermann's determination of free alkali in soaps was unreliable. Heermann replied. Berg also opposed some of Schmatolla's conclusions.

ANALYSIS OF INORGANIC COMPOUNDS.

Metalloids.—The conditions under which it is possible to get an accurate determination of hydrogen peroxide in the presence of potassium persulphate by means of potassium permanganate were given in detail by Friend (*Proc. Chem. Soc.*, **20**, 65, 198; *J. Chem. Soc.*, **85**, 597, 1533). He concluded that the reason for the unsatisfactoriness of the determination under ordinary conditions is the slow interaction of peroxide and persulphate thus: $H_2O_2 + K_2S_2O_8 = K_2SO_4 + H_2SO_4 + O_2$. A colorimetric determination of hydrogen peroxide was devised by Planés (*J. Pharm. Chim.* (6), **20**, 538) depending upon the liberation of a molecule of iodine from potassium iodide by a molecule of peroxide in the presence of dilute sulphuric acid, the color of this iodine solution being compared with that of tenth-normal iodine solution.

To determine the purity of commercial sulphur Ceruti (*Boll. Chim. Farm.*, **43**, 421) dissolved the sulphur of the product in aniline of boiling-point 180–185°, precipitated it with acid and weighed it. Feld (*Z. anal. Chem.*, **42**, 708) gave two methods for the determination of sulphide and chloride together. One is to distil the hydrogen sulphide off with magnesium sulphate in a current of carbon dioxide, receive it in an iodine solution of known strength and then to precipitate the halide in the regular manner with silver nitrate. In the other, both are precipitated with excess of silver salt, the whole made up to definite volume and the excess of silver determined in one portion of the liquid by titration with ammonium sulphocyanate. The precipitate and the rest of the liquid are distilled in a current of carbon dioxide with aluminum turnings and hydrochloric acid, when the conversion of silver sulphide into silver and hydrogen sulphide goes smoothly; the hydrogen sulphide may be determined as in the other method with iodine solution. Total sulphur, when sulphur is present in forms other than sulphide, may be determined by a slight modification of this latter method. Sulphur was determined in calcium carbide by Lidholm (*Z. angew. Chem.*, **17**, 558) by fusing the material over an alcohol flame with five parts of potassium and sodium carbonates and two of ammonium chloride. The melt and crucible were put into a flask and distillation carried on with water and hydrochloric acid in a current of carbon dioxide. The hydrogen sulphide was led into two absorption flasks containing cadmium and zinc acetates and acetic acid, then the sulphides were converted into copper sulphide and ignited to copper oxide. Orloff (*J. russ. phys.-chem. Ges.*, **36**, 1311) proposed a method for the determination of hydrosulphurous acid and one for formalin also.

$$HgI_2.2KI + Na_2S_2O_4 + 4NaOH = Hg + 2NaI + 2KI + 2Na_2SO_3 + 2H_2O$$
$$Hg + I_2 = HgI_2.$$

Ten cc. of the double salt solution (60 grams mercuric chloride

and 260 grams potassium iodide in one liter) were mixed with a potassium hydroxide solution and the solution of the material to be investigated. The mercury was filtered, washed, put into a solution of sodium hydroxide, then excess of tenth-normal iodine solution was added and, after acidification, titrated back with tenth-normal thiosulphate. The formalin method was similar. $HgI_2.2KI + 3KOH + HCOH = Hg + 2KI + HCOOK + 2H_2O$. Pozzi-Escot (*Rev. gen. de Chim.*, **7**, 240) proposed to determine sulphur in easily volatile organic compounds by oxidation with chromyl chloride. He put 1 gram of substance into a 500 cc. flask with 10 to 15 grams of pure dry chromium trioxide and 20 to 25 cc. of hydrochloric acid as pure and as concentrated as possible, then let it stand for thirty minutes and heated to boiling with a return-flow condenser for ten. With excess of chromium trioxide the oxidation is complete. The chromium was reduced with alcohol and the sulphuric acid determined with barium chloride. A new method for the determination of sulphur in iron and steel was proposed by Polsifer (*Chem. News*, **90**, 230), who dissolved the sample in chloric acid, a very little hydrofluoric and lastly hydrochloric acid and filtered the residue, which he then rendered soluble in water and hydrochloric acid by fusion with sodium peroxide. The two solutions were put together and the sulphuric acid precipitated with barium salt. Rossi (*L'Industria chimica*, **6**, 253) determined the amount of sulphuric acid in commercial acetic acid by making use of the fact that the latter is indifferent to methyl orange in alcoholic, formaldehyde or especially acetone solution, so that the sulphuric acid may be titrated with sodium hydroxide in one of these solutions.

Gutbier (*Z. anorg. Chem.*, **41**, 448) found that from compounds in which selenium or tellurium had a valence of 6 the element was not completely precipitated by phosphorous acid, but that from compounds of lower valence the reduction was rapid. Gallo (*Atti R. Accad. dei Lincei Roma* [5], **13**, I, 713; *Gaz. chim. ital.*, **34**, II, 404) electrolyzed tellurium from a solution prepared as follows: The metal was dissolved in concentrated sulphuric acid and warmed to the appearance of white fumes; after cooling, a few cubic centimeters of water boiled and cooled in an atmosphere of carbon dioxide were added, and then 100–150 cc. of a 10 per cent. solution of potassium or sodium pyrophosphate boiled and cooled in carbon dioxide. This solution was slowly heated in a Classen dish to a temperature of 60–62° and electrolyzed at this temperature with a current of 0.025 ampere per sq. dm. and a tension of 1.8 to 2 volts. The end of the reaction was told by the lack of the brown ring in 1 or 2 cc. of the liquid after adding hydrochloric acid and stannous chloride. The precipitate was washed before the current was interrupted.

Baubigny and Chavanne (*C. R.*, **138**, 85; *Bull. Soc. Chim.* (3), **31**, 346) proposed a method for the determination

of chlorine and bromine in organic substances, in which they burned the material with a chromic acid mixture in a special apparatus. The chlorine and bromine were absorbed in alkaline sodium sulphite solution. Iodine, if present, would be oxidized to iodic acid in the chromic acid. The chromic acid mixture consists of 30–40 cc. of sulphuric acid, 1 to 1.5 grams of silver sulphate and 8 to 10 grams of potassium bichromate. Lemaitre (*Mon. scient.* (4), **18,** I, 253) determined the amount of sodium perchlorate in commercial nitrates by fusing the nitrate with sodium sulphite and determining the chloride formed by titration with silver salt, using chromate as indicator, or gravimetrically, the sulphate being first removed by treatment with barium nitrate. $NaClO_4 + 4Na_2SO_3 = 4Na_2SO_4 + NaCl$. Jones (*Chem. News,* **89,** 229) found that primary ammonium carbonate solution gives a sharp separation of silver chloride from silver bromide. A simple test for, and method of determination of hypochlorous acid was given by Klimenko (*Z. anal. Chem.,* **42,** 718). This acid and potassium iodide give free iodine, and when hydrochloric acid is then added more iodine, equal in amount to the first, is set free. Chlorine water with potassium iodide yields iodine, but no more if hydrochloric acid be added. If the 4 or 8 per cent. solution of potassium iodide be run into the solution containing hypochlorous acid, the amounts of iodine liberated before and after the hydrochloric acid addition are practically identical. Pontius (*Chem.-Ztg.,* **28,** 59) determined the active chlorine in bleaching-powder, etc., by using the principle that hypochlorous acid in the presence of primary sodium carbonate oxidizes iodide to iodate. He added the chloride of lime solution to some primary sodium carbonate in a dish, then some starch paste and titrated with potassium iodide solution till the next drop caused no blue color. Thilo (*Chem.-Ztg.,* **28,** 866) founded a method for the determination of iodine in the presence of bromine and chlorine upon the observation that on gradual addition of silver salt solution to a solution containing all three halides, iodine is first precipitated completely, and further that iodine will convert silver bromide and chloride into iodide. The end-point of the iodine precipitation, carried out with silver solution of known strength, is shown when a drop of the solution no longer gives a dark spot of palladious iodide on filter-paper freshly dipped in palladious chloride solution. Hennecke (*Pharm. Ztg.,* **49,** 957) titrated iodine in chloroform solution directly with tenth-normal sodium thiosulphate in order to avoid the decomposition of iodine monochloride, which it may contain, thus: $ICl + KI = I_2 + KCl$. Froidevaux (*J. Pharm. Chim.* (6), **20,** 11) offered a method for the detection of fluorine in meat and sausages. He ignited the meat with soda and dissolved the residue in a little boiling water. The filtrate he treated with 2 to 3 cc. of hydrochloric acid and a few drops of helianthine, then saturated ammonium acetate solution till a yellow color was

obtained. The addition now of 1 to 2 cc. of 20 per cent. calcium chloride solution would cause a turbidity, if fluorides were present.

Jalowetz (*Allgem. Z. f. Bierbrauerei und Malzfabrikat.*, May, 1904) and Barelt and Schonewald (*Wochschr. f. Brauerei*, **21**, 523, 793) gave figures to show the effect of different kinds of glass upon the results in the Kjeldahl determinations, and the effect is considerable. Brame (*Osterr. Z. f. Berg.-Hutt.*, **52**, 491) gave a rapid method for the determination of nitrogen in iron and steel, in which he obtained the nitrogen as ammonia, passed it into Nessler's reagent and compared it with standard color. Büeler de Florin (*Chem.-Ztg.*, **28**, 1264) recommended for a color scale in working with Nessler's reagent yellow glass plates instead of solutions of known ammonia content. Effront (*Mon. scient.* (4), **18**, 669) based a method for the determination of ammonia and proteid nitrogen in water on the reduction of alkali hypochlorite by ammonia and by albuminous substances, according to this equation: $2NH_3 + 3CaOCl_2 = 3CaCl_2 + 3H_2O + N_2$. He titrated the chloride of lime solution before and after treatment with the water. Another article containing the same principle was published by the same author (*Ber.*, **37**, 4290). Jean (*Ann. Chim. anal. appl.*, **9**, 257) proposed a rapid titration for ammonium sulphate and ammonium chloride. He dissolved the salt in water, added a known amount of a sodium hydroxide solution, made up to a definite volume and titrated one portion directly with half-normal oxalic acid, using lacmoid for indicator. Another portion was diluted and boiled for half an hour, then titrated with the acid. From the difference between these two acid values the nitrogen or the ammonium salts can be calculated. Riegler (*Z. anal. Chem.*, **42**, 677) used the compound $NH_4H_2(IO_3)_3$, which is insoluble in dilute alcohol, as the basis of a gravimetric determination of ammonia. The salt was precipitated by a large excess of iodic acid and was dried over sulphuric acid to constant weight. Or the determination could be made volumetric by treating the precipitated salt with 2 per cent. hydrazine sulphate solution in a nitrometer of some sort and measuring the evolved nitrogen. Sellier (*Bull. de l'Assoc. d. Chim. de Sucr. et Dist.*, **21**, 1063, 1115, 1223) reviewed critically the methods for the determination of ammonia in vegetable products, especially in beets and in the products of the sugar factory and the distillery, deciding that the method of Boussingault of distilling in a vacuum below 40° from magnesium oxide is the most satisfactory. Stähler (*Ber.*, **37**, 4732) found that hydroxylamine could be determined volumetrically by reducing it to ammonia with titanium trichloride or trisulphate, and titrating the excess of trivalent titanium with permanganate, ferric chloride or potassium chlorate. A method for the simultaneous detection of nitrous and nitric acids and for their approximate quantitative determination was offered by Raikow (*Osterr. Chem. Ztg.*, **7**, 557). It depends upon

the behavior of the two acids toward diphenylamine in concentrated sulphuric and especially in syrupy phosphoric acid solution. He dissolved 0.2 gram of diphenylamine in 100 cc. of pure concentrated sulphuric acid or of syrupy phosphoric acid, placed 0.5 cc. of this solution in a little flat-bottomed porcelain dish at the edge and added a drop ($^1/_{30}$ cc.) of the liquid to be tested so that the two liquids would run together. Nitrites give a blue color in either solution, nitrates a blue color much more slowly in sulphuric acid solution, and in phosphoric acid solution, characteristic black points with sharply defined edges which are visible even in the solution colored blue by nitrites. The limits of sensitiveness of the reaction are for the sulphuric acid solution 0.0000003 gram potassium nitrate and 0.0000005 gram sodium nitrite and for the phosphoric acid solution 0.0025 gram of nitrate and 0.0000006 gram nitrite. By diluting the solution to be investigated with known amounts of water till under the above conditions the limits of sensitiveness are reached one can calculate the nitrate or nitrite content. Debourdeaux (*C. R.*, **136,** 1668; *Bull. Soc. Chim.* (3), **31,** 3) gave a new volumetric method for the determination of nitric acid. He heated about 0.5 gram of the nitrate in a flask provided with a return flow condenser with 50 cc. of a solution containing 35–40 grams of crystallized oxalic acid, 50 grams of crystallized manganese sulphate and 120 cc. of 66 per cent. sulphuric acid in one liter. The heating was done on a water-bath and after the gas evolution the undecomposed oxalic acid was titrated with permanganate. He (*Compt. rend.*, **138,** 147) applied the same principle to the determination of chlorates, bromates and iodates. Blunt (*The Analyst*, **28,** 313) found that water containing nitrites would give a yellow tint when treated with potassium ferrocyanide.

Lidholm (*Z. angew. Chem.*, **17,** 1452) burned the phosphorus in calcium carbide to phosphoric acid. He provided a flask with a three-holed stopper carrying a dropping funnel, a tube through which hydrogen could enter and a return-flow condenser connected with the simple metal burner having a hole so fine that the acetylene flame would not smoke. The products of combustion were caught in a cylinder 32 cm. long and 5 cm. wide, ending in a 5 mm. tube which was connected with a gas wash-bottle and then with a suction-pump. The carbide was weighed and placed in the flask, then the stream of hydrogen started. The gas was lighted after the air was driven out, then 30 cc. of alcohol were added dropwise to the carbide in the flask, then water. After the gas evolution had stopped, hydrochloric acid was added and the contents of the flask boiled. When the hydrogen flame burned colorless again it was extinguished and the glass cylinder, tubes and wash-bottle were washed with warm ammonia, then with water. The solution was filtered to separate out silica and the phosphoric acid determined as usual with magnesia mixture. Christomanos

(*Z. anorg. Chem.*, **41**, 305) studied the formation of the phosphides of copper and their oxidation, and evolved therefrom a method for the quantitative determination of phosphorus in solution. He weighed the ether or benzene solution of phosphorus into a weighed glass flask, then shook it for some minutes with an excess of a 10 per cent. solution of copper nitrate. A black precipitate was obtained of one of the phosphides of copper. This was heated for fifteen or twenty minutes on a water-bath to cause the precipitate to settle and to drive off the ether or benzene. Then he added to the warm mixture of precipitate and liquid on the water-bath bromine a little at a time with continual shaking; the reaction was violent with the formation of cuprous bromide, perhaps also copper, and phosphorus tribromide which decomposed into phosphorous acid and some phosphoric. He had finally a dark green solution which contained some cupric bromide, all the phosphorus as the two acids, some nitric acid and excess of bromine. The solution was concentrated on the sand-bath with nitric acid to remove bromine and to oxidize all the phosphorous to phosphoric acid, then concentrated further to remove the nitric acid. The phosphoric acid was determined with magnesia mixture. A method for the determination of arsenic which does not depend upon mirrors or color reactions was devised by Cowley and Catford (*Pharm. J.* (4), **19**, 897), who treated 10 cc. of the liquid to be investigated with 2 cc. of hydrochloric acid in a test-tube, sunk a copper spiral most of its length into the liquid, placed the tube in a gently boiling salt-water bath and left it there for an hour. Then they pushed the rest of the spiral down into the liquid and observed whether it was bright after ten minutes, which afforded evidence that all the arsenic had been precipitated. The spiral was now placed in a dish, the arsenic dissolved in bromine water containing some hydrobromic acid, 1 cc. of caustic potash solution added, the mixture boiled to precipitate the dissolved copper and filtered. In the filtrate they reduced the arsenic acid to arsenious and titrated with iodine solution. Pozzi (*L'Industria chimica*, **6**, 144) offered a rapid indirect method for the determination of arsenic, based upon this reaction for dilute solutions: $2AsH_3 + 12AgNO_3 + H_2O = As_2O_3 + 12HNO_3 + 12Ag$. He regulated the flow of hydrogen from his Marsh apparatus to not more than twenty bubbles per minute, added the solution to be analyzed and caught the arsine in two vessels containing 20 cc. of tenth-normal silver nitrate and 1 cc. of ammonia. After three or four hours he determined in 10 cc. of the filtered solution, after acidification with nitric acid, the amount of undecomposed silver nitrate by means of potassium sulphocyanate, using ferric sulphate for indicator. According to Pozzi, 0.1 mg. of arsenic may be detected in this way. Vizern and Guillot (*Ann. Chim. anal. appl.*, **9**, 248) gave this method of detecting arsenic in the crude glycerol of the soap industry. They oxidized 10 cc. of

dilute glycerol with 2 grams of hydrogen peroxide of 10–12 per cent. volume content and 2 cc. of hydrochloric acid and a minute's boiling. They then let the mixture cool, put it completely into a large test-tube and added 1 gram of pure zinc with a little copper sulphate. The test-tube was next covered with mercuric chloride paper. After fifteen minutes the under side of the paper would be colored yellow, if there were 1 part of arsenic in 1,000,000 of material. Bougault (*J. Pharm. Chim.* (6), **18,** 509, 545; *Compt. rend.*, **137,** 794) concluded that the presence of antimony trioxide in kermes is more and more doubtful, and that the substance is practically a mixture of antimony trisulphide and acid sodium pyroantimoniate.

A new melting medium for use in the indirect dry way of determining carbon dioxide was proposed by Lutz and Tschischikow (*J. russ. phys.-chem. Ges.*, **36,** 1274). They used sodium metaphosphate and gave its advantages over borax, potassium bichromate and silica. The error caused by its change in weight is negligible, the time required for the operation is short and it may be used even for natural carbonates. It may also be used for the determination of the nitrogen pentoxide of nitrates. The potassium metaphosphate or a mixture of it with the sodium salt does not give satisfactory results. Baroni (*Giorn. Farm. Chim.*, **53,** 481) proposed an easy method of testing the neutrality of glass of vessels. He used neutral solutions of morphine hydrochloride (1 to 2 per cent.), strychnine nitrate (0.5 per cent.), and mercuric chloride (1 per cent.), fused them in the glass to be tested and heated for half an hour in an autoclave at 112°. If the glass is neutral each solution remains unchanged. But if even small amounts of sodium oxide are given up, the morphine salt solution is colored brown with deposition of crystals of the free alkaloid on the sides of the vessel; free strychnine is deposited from the solution of its salt, and yellow, red or brown oxides, finally becoming a brown precipitate, are formed in the mercury salt solution. Van Rijn (*Pharm. Weekblad*, **41,** 1025) determined the alkalinity of glass by simply cleaning it with hydrochloric acid and water, then filling it with distilled water containing phenolphthalein. There must be no reddening after fourteen days. Lucchese (*Ann. Chim. anal. appl.*, **9,** 450, 452) analyzed ferrosilicon by fusion with two or four parts of soda and the same amount of sodium peroxide in a platinum crucible, taking care that pieces of the ferrosilicon did not rest on the bottom of the crucible, and heating very cautiously. The silica was precipitated as usual from the water solution of the melt by means of hydrochloric acid. He gave also a rapid method for the analysis of the same compound, in which he drove off the silicon by evaporating the material to dryness a couple of times with a very little water, 1 cc. of hydrofluoric acid and 1 cc. of nitric acid. The iron remains as ferric oxide, with small amounts of im-

purities. He weighed the iron oxide, calculated it to metallic iron, and obtained the silicon by difference, neglecting the impurities. Cantoni (*Ann. Chim. anal. appl.*, **9,** 203) rendered his iron-silicon compound soluble by gentle fusion with sodium peroxide, using a copper crucible and removing the copper which dissolved by precipitation with hydrogen sulphide after he had separated the silica.

Metals.—A new method of procedure for the determination of alkalies especially in plants was proposed by Neubauer (*Z. anal. Chem.*, **43,** 14), who precipitated the phosphoric acid, iron, aluminum and magnesium oxides by means of a saturated solution of calcium hydroxide, then the lime with oxalic acid and finally weighed the alkalies as sulphate. Stolberg (*Z. angew. Chem.*, **17,** 741, 769) separated calcium and magnesium by converting both into sulphates, adding a little water to dissolve magnesium sulphate, then a mixture of methyl and ethyl alcohols to throw out the traces of calcium sulphate dissolved. Coehn and Kettembeil (*Z. anorg. Chem.*, **38,** 198) found that the alkaline earth metals could be separated by electrolysis. They tried saturated solutions of the chlorides with varying voltages and determined the current in each case. The voltages were measured against a calomel electrode at 15–18°. As potential differences in the beginning of amalgam formation of the three metals in saturated chloride solution they found between barium and strontium 0.2 volt, between strontium and calcium 0.25 and between barium and calcium 0.45. The differences were still greater when equal concentrations of the three salts were taken. Reichard (*Chem. Ztg.*, **28,** 16) observed that barium, calcium, sodium and potassium peroxides would cause the yellow color in a solution of titanium dioxide in concentrated sulphuric acid, just as hydrogen peroxide does, but that lead and manganese dioxides, cobaltic and nickelic oxides would not. Authenrieth (*Ber.*, **37,** 3882) observed that strontium chromate crystallizes well and is thrown out of solution under conditions that will cause an amorphous precipitation of the barium salt and no precipitation of the calcium salt. He used the reaction for the microchemical detection of strontium and its chromate. He described two modifications. He stated also that he has never found the strontium reaction described by Behrens.

A separation of aluminum from iron was given by Leclere (*C. R.*, **138,** 146). He added to the fairly dilute solution containing a slight excess of sulphuric acid ammonium hyposulphite to reduce the iron, then a great excess of ammonium formate and of hyposulphite and heated to boiling. Aluminum was precipitated as basic formate and was determined by ignition to the oxide. Iron and chromium were separated by Southerden (*Chem. News*, **89,** 183) by melting the dry precipitate of the two in a test-tube with potassium nitrate and adding primary potas-

sium sulphate in small amounts. Chromium is oxidized to chromate. Glasmann (*Z. anal. Chem.*, **43,** 506) gave an oxidimetric method for determining iron and chromium together. The solution was reduced by means of sulphur dioxide in a flask provided with a Bunsen valve, this gas was driven out by boiling and leading in carbon dioxide and the reduced iron was titrated with permanganate. The solution was reduced now with sulphuric acid and zinc, warmed on a sand-bath till it had a constant blue color, indicating the reduction from chromic to chromous oxide, then excess of permanganate was added and the excess titrated with a ferrous salt. Leuba (*Ann. Chim. anal. appl.*, **9,** 303) in his chromite analyses used nitric acid to dissolve the soda melt, but the iron and aluminum hydroxides obtained from this solution with ammonia always contained some chromium. He found this to be due to a reducing action of nitric acid on chromates, it being possible to decompose as much as 9 per cent. of the bichromate with formation of chromic salt by repeated evaporation with nitric acid. The same thing is true with acetic acid. Moulin (*Bull. Soc. Chim.* (3), **31,** 295, 296) based a colorimetric method for the determination of chromium upon the color reaction mentioned by Cazeneuve, that chromium trioxide or a chromate gives with the acetate of diphenylcarbazide a magnificent purple solution. The chromium of the sample was oxidized to chromate by means of hydrogen peroxide and caustic potash, and the liquid neutralized with acetic acid and diluted to 100 or 200 cc. Into each of a series of 100 cc. cylinders was put 2 cc. of the diphenylcarbazide solution (2 grams carbazide, 10 grams acetic acid and 90 per cent. alcohol added to 200 cc.) and 70 cc. of water. Then increasing amounts of a solution of known chromic acid content were added to some of the cylinders, and to others definite amounts of the solution to be tested. Then the cylinders were all filled to 100 cc. and compared in a Dubosc colorimeter after twenty minutes. Moulin described the color reaction in detail and analyzed the products. To the violet compound he ascribed the formula $C_{41}H_{44}N_{10}O_{16}Cr$. Nicolardot (*C. R.*, **138,** 810) separated chromium from vanadium as chlorchromic acid. He melted the sample with four parts of potassium chlorate and one of sodium carbonate, removed small amounts of iron and manganese in the usual manner, then concentrated, dried and melted the salt mass. This was placed in a flask which was connected with a small wash vessel containing sulphuric acid to stop any vanadium that might be carried over, then with a flask filled with dilute sodium hydroxide solution and with a suction-pump. Next fuming sulphuric acid was allowed to flow into the flask through a dropping funnel, at the same time carefully drawing air or hydrochloric acid gas through the apparatus and warming the flask and wash-vessel with sulphuric acid to 60° till the red fumes ceased. Carcano and Namias (*Boll. Chim. Farm.*, **43,** 54)

based a volumetric method for the determination of iron in the ferric condition upon this equation: $Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + I_2$. They prevented reoxidation of the ferrous chloride by collecting the iodine in chloroform. The ferric iron solution was diluted till it contained 1 to 2 per cent. of iron, neutralized with sodium carbonate, then concentrated hydrochloric acid was added till the solution contained 5 to 10 per cent. of it, then 2 grams of potassium iodide. After a little standing they added 5 to 10 grams of chloroform and determined the iodine by means of thiosulphate and starch paste. Hollard (*Ann. Chim. anal. appl.*, **9,** 220; *Bull. Soc. Chim.* (3), **31,** 904) stated that he had already used the Carcano and Namias method for the determination of impurities in copper. Tarugi and Silvatici (*Boll. Chim. Farm.*, **43,** 637) gave a new method for the colorimetric determination of iron. One molecule of ferric chloride requires always three molecules of potassium oxalate to decolorize it, and potassium sulphocyanate may be added to the solution for an indicator without influencing the reaction. They recommended the preparation of a fresh typical comparison solution each time titrations are to be made; 5 cc. of tenth-normal ferric chloride, a few drops of potassium sulphocyanate solution and 15 cc. of tenth-normal potassium oxalate. Urbain and Lacombe (*C. R.*, **137,** 792; **138,** 84, 627) in a series of papers gave the results of using the magnesium bismuth double nitrate to help the fractional separation by crystallization of the magnesium double nitrates of the samarium-gadolinium group of rare earths. Lacombe (*Bull. Soc. Chim.* (3), **31,** 570) showed that the double nitrates of the rare earths and manganese possessed advantages for certain separations, notably that of neodymium from praseodymium.

Baumert and Holdefleiss (*Z. f. Unters. Nahr.-Genussm.*, **8,** 177) proposed a method for the detection and determination of manganese in drinking-water. It is a reversal of Winkler's method for the determination of oxygen in water, the equations being as follows:

$$2Mn(OH)_2 + O + H_2O = 2Mn(OH)_3$$

$$2Mn(OH)_3 + 6HCl + 2KI = 2MnCl_2 + 2KCl + 6H_2O + I_2$$

Debourdeaux (*C. R.*, **138,** 88) gave a method whereby the chlorine value and also the hydrochloric acid value (the amount of acid necessary to neutralize the oxide and to free the chlorine) may be determined in one operation instead of in two as formerly. He made use of the decomposition of oxalic acid by the higher oxides of manganese in the presence of dilute sulphuric acid. The equations for manganese dioxide are:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

$$MnO_2 + C_2H_2O_4.2H_2O + H_2SO_4 = MnSO_4 + 2CO_2 + 4H_2O$$

Those for the other oxides are similar. One molecule of oxalic acid decomposed corresponds to one molecule of chlorine. He

heated to gentle boiling in a flask with return-flow condenser the manganese oxides with 50 cc. of a solution composed of 35–40 grams of crystallized oxalic acid, 120 cc. of 66 per cent. sulphuric acid and water to one liter till the oxides were dissolved. Then he diluted this solution and also 50 cc. of the oxalic-sulphuric acid solution each to 200 cc. and determined the oxalic acid in 150 cc. of each by means of permanganate. The chlorine value of the oxides was calculated from the difference in these two oxalic acid values. For the hydrochloric acid value he titrated in the last 50 cc. of each solution the total free oxalic and sulphuric acids, using ammonia and fluorescein. The difference gave the sum of the decomposed oxalic and the combined sulphuric acid and by calculation the hydrochloric acid value desired. A method for the separation of cobalt and nickel from one another and from other metals was patented by Frasch (*Chem. Centrbl.*, 1904, I, 1585). The solution containing these metals was treated with excess of ammonia, filtered and the solution treated with alkali chloride, when the cobalt and nickel are precipitated. He separated out the precipitate and treated it with water, when the nickel ammonia chloride dissolved, while the cobalt ammonia chloride decomposed into hydroxide.

$$Co(NH_3)_2Cl_2.4NH_3 + 2H_2O = Co(OH)_2 + 2NH_4Cl + 4NH_3.$$

Muller (*Bull. Soc. Chim.* (3), **31,** 1300) found that lead and antimony may be satisfactorily determined as sulphides by precipitation from hot acid solutions with hydrogen sulphide, collecting the precipitate on a weighed filter, washing successively with hydrogen sulphide water, 95 per cent. alcohol, a mixture of equal volumes of 95 per cent. alcohol, ether and carbon bisulphide and finally with absolute ether, then drying in a vacuum over sulphuric acid. Rupp (*Z. anal. Chem.*, **42,** 732) tested the action of hydrogen peroxide upon lead, manganese and bismuth salts and found that the bismuth precipitate was bismuthyl hydroxide, while the precipitates of lead and manganese were not of constant composition. Corradi (*Boll. Chim. Farm.*, **43,** 424) determined mercury volumetrically by titrating a known solution of the mercury compound with known potassium iodide solution till the mercuric iodide dissolved. Rose recommended that the end reaction of the Volhard silver determination be sharpened by filtering near the end of the reaction and finishing the titration in the clear filtrate, but Hoitsema (*Z. angew. Chem.*, **17,** 647) pointed out that this causes an error in the results, for the soluble salts can not be washed entirely out of the silver sulphocyanate. Thiel (*Allgemeine Chem. Ztg.*, 4, No. 49) detected silver in the presence of mercurous compounds by treating the precipitated chlorides with bromine water, when the mercury dissolves.

A new volumetric method for the determination of copper was recommended by Griggi (*Boll. Chim. Farm.*, **43,** 392). He

titrated the copper salt with a solution containing 1.39 grams of hydroxylamine hydrochloride and 5.6 grams of caustic potash made up to one liter with cold distilled water.

$$(NH_2OH)_2.2HCl + 4(CuSO_4 + 5H_2O) + 10KOH = 2Cu_2O + N_2O + 2KCl + 4K_2SO_4 + 29H_2O.$$

The sulphates of many other metals have a disturbing influence. Cloud (*J. Soc. Chem. Ind.*, **23,** 523) based a determination of small amounts of bismuth upon the fact that lead iodide precipitated in the presence of bismuth is colored more or less dark orange, according to the amount of the latter present. The lead-free solution was treated with 5 cc. of a solution of lead nitrate containing 6 grams of lead per liter and shaken with 25 cc. of a solution of 8.75 grams of potassium iodide per liter, then allowed to stand for fifteen or twenty minutes. The color of the precipitate was then compared with other precipitates which contained known amounts of bismuth. Reichard (*Chem. Ztg.*, **28,** 1024) observed that a drop of bismuth chloride solution would give a magnificent red color with solid brucine or a concentrated solution of brucine, and that the color would remain on evaporation to dryness.

Desvergnes (*Ann. Chim. anal. appl.*, **9,** 321) proposed to determine tungsten by precipitating it from a boiling solution containing it in the form of tungstate by means of a solution of mercuric nitrate containing suspended mercuric oxide. The mixture was again brought to boiling, allowed to settle and the precipitate of mercuric tungstate with oxide ignited. Frabot (*Ibid.*, **9,** 371) noticed independently of Riegler that tungstic acid or Moreigne's phosphotungstic acid reagent and caustic soda would give with uric acid a magnificent blue color. A volumetric method for the determination of tungsten was founded by Kuklin (*Stahl und Eisen*, **24,** 27) upon the fact that metatungstic acid is reduced to tungsten dioxide by excess of zinc, and that this may be oxidized again by permanganate to tungstic acid.

$$5WO_2 + Mn_2O_7 = 5WO_3 + 2MnO.$$

For tungsten in steel he dissolved 2 grams in a mixture of concentrated sulphuric and phosphoric acids and three times as much water, then he added enough permanganate solution so that the solution was colored permanently red, warmed, then cooled and measured it. Half of this solution was treated with sulphuric acid and zinc and heated till the solution took on a port wine color, then allowed to cool in a current of carbon dioxide. After cooling and filtering off the zinc the solution was titrated with permanganate to a rose color. This gave the amount of permanganate needed to oxidize both iron and tungsten dioxide. In the other portion Kuklin determined by the Reinhardt method or by means of stannous chloride and iodine the amount of per-

manganate needed for the iron alone. A drop of an alcoholic solution of diphenylcarbazide added to a solution of sodium or ammonium molybdate in 30–40 cc. of water acidified with two or three drops of hydrochloric acid gives a magnificent violet color, according to Lecocq (*Bull. de l'Assoc. Belge des Chim.*, **17,** 412). Giolitti (*Gaz. chim. ital.*, **34,** II, 166) determined uranium by reducing the salt, if uranyl, and then precipitating the tetravalent uranium by means of hydrofluoric acid in a platinum dish, washing by decantation, filtering through a rubber funnel and igniting in an open crucible to uranous-uranic oxide. Glasmann (*Ber.*, **37,** 189; *J. russ. phys.-chem. Ges.*, **36,** 317) used the following reaction for the iodometric determination of uranium:

$$3UO_2(NO_3)_2 + 5KI + KIO_3 + 3H_2O = 3UO_2(OH)_2 + 6KNO_3 + 3I_2.$$

The iodine is distilled into a receiver and titrated with thiosulphate. Dreher (*Centrbl.*, 1904, II, 67) patented a method for the separation of titanic acid from mixtures of it with metals like iron, aluminum, etc. Instead of reducing the solution in mineral acid by means of sulphur dioxide he used such metals (tin, zinc, iron, sodium amalgam) as would give hydrogen with the acid of the solution (which might be sulphuric or alkali bisulphate, hydrochloric, hydrofluoric or an organic acid like oxalic). The acid titanium solution could also be electrolyzed at the cathode where hydrogen is evolved. The titanic acid present would be thrown out as a bluish precipitate, if the solution were weakly acid or on approximate neutralization. This lower form of oxidation is changed again in the air or by an oxidizing agent to the white titanic acid. Dreher stated that this titanic acid is free from the metals and that it is precipitated in the easily soluble form. Campagne (*Bull. Soc. Chim.* (3), **31,** 962) gave a method of detection and a volumetric method of determining vanadium and chromium together. The solid was fused with a mixture of equal parts of sodium nitrate and carbonate, the mass extracted with water, filtered, the filtrate acidified with sulphuric acid and shaken with a few cubic centimeters of hydrogen peroxide and ether. With both metals present the aqueous solution would be red, the ether blue. For the volumetric determination the solution was repeatedly evaporated with hydrochloric acid to form vanadyl dichloride ($VOCl_2$). Free sulphuric acid must be absent. At the end of the reduction the substance was treated with 10 cc. of pure sulphuric acid and heated on a sand-bath till white fumes appeared. Chromic sulphate and hypovanadic sulphate ($V_2O_2(SO_4)_2$) are formed. This was taken up with water and titrated at the ordinary temperature with permanganate to oxidize the vanadium.

$$5V_2O_2(SO_4)_2 + 2KMnO_4 + 8H_2SO_4 = 5V_2O_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

At the end of the titration an excess of 10 per cent. permanganate

was added and the solution boiled to oxidize the chromium to chromate, the excess of permanganate removed by pieces of filter-paper and the solution filtered after cooling. The chromium was then reduced by means of a known excess of ferrous ammonium sulphate solution and the excess titrated back with permanganate. In reality instead of titrating the excess of ferrous salt the amount of vanadyl sulphate ($V_2O_2(SO_4)_3$) reduced by it to hypovanadic sulphate ($V_2O_2(SO_4)_2$) was titrated. Glasmann (*J. russ. phys.-chem. Ges.*, **36**, 314) separated vanadium from iron and aluminum by means of potassium iodide and iodate and removal of the precipitated iodine with sodium thiosulphate.

$$V_2O_5 + 4HI = V_2O_3 + 2H_2O + 2I_2.$$

$$Al_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Al(OH)_3 + 3K_2SO_4 + 3I_2.$$

A method for the determination of tin in tin plate was given by Angenot (*Z. angew. Chem.*, **17**, 521). He cut the plate into pieces about 1 cm. square, heated them in a little iron crucible to quiet fusion for ten minutes with twice as much sodium peroxide, allowed the mass to cool and dissolved it in a covered beaker in 100 cc. of cold water, washed into a 250 cc. flask, filled to the mark and filtered. He acidified 200 cc. of the filtrate with dilute sulphuric acid (1:2), boiled for five minutes, washed the precipitate, then ignited it to stannic oxide.

Donau (*Monatsh. Chem.*, **25**, 545, 913) gave a microchemical test for gold, and the colors of the borax bead caused by some of the noble metals in colloidal solution. Silk fiber, prepared from crude silk by three or four hours' treatment with 10 per cent. potassium or sodium hydroxide solution, washing and mordanting with stannous chloride and pyrogallol, gives with specially prepared chlorauric acid solutions red colors by means of which Donau said the delicacy of the present microchemical tests could be increased 1000 times. The color is not destroyed by acids or bases but is by chlorine or bromine, which shows the color to be due to gold. The red color is due to colloidal gold; blue or dark colors are due to more or less coarse gold particles. Gold gives a ruby-red color to the borax bead, silver a yellow and platinum a fawn-color. A volumetric determination of platinum resting on the difficult solubility of thallous chlorplatinate was given by Rupp (*Arch. der Pharm.*, **242**, 143). He used a 2 to 2.5 per cent. solution of thallous nitrate standardized against potassium chromate thus: Ten cc. of a 4 per cent. solution of the chromate of known thiosulphate titer were treated in a 100 cc. flask with water and about 1 gram of precipitated calcium carbonate, 10 cc. of thallium solution were added, the volume made up to 100 cc. and the whole mixed and filtered. Of the filtrate 25 cc. were treated with 50 cc. of water, 1 to 2 grams of potassium iodide, about 5 cc. of 25 per cent. hydrochloric acid and titrated after five minutes with twentieth-normal thiosulphate solution. The

platinum solution, which may contain only a very little hydrochloric acid, was put in a 50 or 100 cc. flask with a measured excess of the thallium solution, allowed to stand for an hour in the cold, made up to the volume, filtered through a double filter and the excess of thallium determined as above in 25 or 50 cc. of the filtrate.

Hollard and Bertiaux (*Bull. Soc. Chim.* (3), **31,** 102, 900, 1124, 1128, 1131; *C. R.*, **138,** 1605, 139, 366) have published half a dozen articles dealing largely with electrolytic separations of these elements: Copper, arsenic and antimony, nickel and zinc, zinc and iron, bismuth and copper and bismuth and lead; also the analyses of commercial lead and tin, which they accomplished largely by electrolytic methods.

Hydrazine sulphate was proposed many times as a reagent useful in making quantitative determinations of various elements, most of the methods being volumetric. The collection follows. Roberto and Roncali (*L'Industria chimica*, **6,** 93, 178) used it to determine oxidizing substances, such as bleaching-powder, permanganate and bichromate.

$$N_2H_4.H_2SO_4 + Cl_2 = N_2 + 4HCl + H_2SO_4.$$
$$N_2H_4.H_2SO_4 + O_2 = N_2 + 2H_2O + H_2SO_4.$$

For the chlorine in bleaching-powder they put 100 cc. of water, 2 to 3 grams of hydrazine sulphate and 30 cc. of dilute sulphuric acid into a flask which was closed by a cork carrying a delivery tube and a funnel tube. The contents of the flask were brought to boiling, and after air was driven out of the flask, 100 cc. of a solution equivalent to 1 gram of bleaching-powder were added with continued boiling, then finally 30–40 cc. of water. The nitrogen was measured as usual and the chlorine calculated. The other two determinations were similar. Another oxidizing agent, potassium persulphate, was similarly determined by Pannain (*Gaz. chim. ital.*, **34,** I, 500). He used a Lunge nitrometer, and set the hydrazine free by concentrated caustic potash.

$$2K_2S_2O_8 + N_2H_4.H_2SO_4 + 6KOH = 5K_2SO_4 + N_2 + 6H_2O.$$

The Riegler (*Z. anal. Chem.*, **42,** 677) determination of ammonia by precipitation of monoammonium triiodate and subsequent treatment of the precipitate with hydrazine sulphate has already been mentioned. This author (*Ibid.*, **43,** 205) again recommended hydrazine sulphate as a means of determining gasometrically calcium, strontium, barium and potassium, also copper. He first precipitated these elements as iodates and then treated the iodates with hydrazine sulphate.

$$Ca(IO_3)_2 + 3N_2H_4.H_2SO_4 = CaSO_4 + 2HI + 6H_2O + 3N_2.$$

Rimini (*Atti R. Accad. dei Lincei Roma* (5), **12,** II, 376; *Gaz. chim. ital.*, **34,** I, 224) determined hydrazine itself by the nitrogen evolved when the hydrazine salt was treated with mercuric

chloride and caustic potash. A molecule of hydrazine salt yields a molecule of nitrogen. The method might be used for mercury. De Girard and de Saporta (*Bull. Soc. Chim.* (3), **31,** 905) gave again the copper determination of Purgotti, using hydrazine sulphate in alkaline solution, and corrected his equation. They suggested the use of the method for the determination of glucose, the cuprous oxide obtained in the usual manner being dissolved up and oxidized, then determined volumetrically. They gave also a direct determination of sodium nitrite.

$$2NaNO_2 + N_2H_4.H_2SO_4 = N_2 + Na_2SO_4 + 2NOH + 2H_2O.$$

Gutbier (*Sitzungsber. d. phys. med. Soc.*, 1904, p. 130) recommended hydrazine sulphate as a means of reducing tellurium for the quantitative determination, and with Metzner and Lohmann (*Z. anorg. Chem.*, **41,** 291) used a hydrazine salt for the reduction of selenium. Jannasch with Bettges, with Rostosky and with Stephan (*Ber.*, **37,** 1980, 2210, 2219 and 2441) used hydrazine salts for the separation of mercury from molybdenum and tungsten, of palladium from nearly all other metals and of platinum likewise from other metals.

NOTE.

On the Detection of Nickel.—The potassium nitrite test for cobalt in presence of other metals, especially nickel, orginally proposed by Fischer,[1] is not very generally used in qualitative analysis, owing probably to the fact that at least twenty-four hours is required to effect complete removal of the cobalt.

Since cobalt is usually more readily detected than is nickel, it may be of interest to give the following modification of Fischer's method by which immediate and complete removal of cobalt can be effected. Since, however, pure nickel solutions give precipitates with this method, which, though slight, could readily be mistaken for cobalt, this test is not applicable for detection of the latter element, and is proposed only as a means for the rapid removal of cobalt, preliminary to testing for nickel.

The method depends on the well-known fact that potassium cobaltinitrite is much less soluble in strong solutions of potassium salts than in water. The procedure is as follows: A portion of the solution is tested for cobalt. In case cobalt is found the remainder, which must be neutral or alkaline, is saturated with potassium chloride, leaving an excess of the solid salt present, and treated with either a little solid potassium nitrite or with

[1] Pogg. *Ann.*, **74,** 124 (1849).

1 or 2 cc. of a saturated solution of this salt. The solution is then acidified with acetic acid and agitated for half a minute. This treatment completely precipitates the cobalt at once, together with a small amount of nickel, if this was originally present in large amount. The solution is now filtered and tested for nickel with ammonium sulphide. A black precipitate or coloration indicates nickel, which may be confirmed with the bead test.

Since the precipitate obtained in this method of precipitation is extremely fine, it is quite difficult to filter clear unless the solution containing it be previously shaken with 5 to 6 grams of some insoluble powder, preferably barium sulphate, when filtration is not at all difficult.

The modification of Fischer's method above described affords probably the most rapid process for the complete removal of cobalt from nickel solutions where it is desired to test for the latter element by reactions with which cobalt interferes.

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NEW BOOKS.

A TEXT-BOOK OF CHEMICAL ARITHMETIC. By HORACE L. WELLS, M.A., Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. First edition, first thousand. New York: John Wiley & Sons. London: Chapman & Hall, Limited. 1905. 12mo. vii + 169 pp. Cloth, $1.25.

Although intended especially for students of quantitative analysis, this little book may be read with profit by chemists generally. It gives a clear discussion of the errors of weighing, etc., and the resultant errors in calculations in which the figures found are involved. The futility of carrying arithmetical processes to uncertain decimal points is pointed out, and in this connection abbreviated methods of multiplication and division are explained. Part II shows how to calculate atomic weights, compositions from formulas and *vice versa*, factors and the results of gravimetric analyses in simple cases and also where mixtures and indirect methods are involved. Parts III and IV give discussions of calculations relating to gases and to volumetric analysis, respectively. The latter includes the standardization and adjustment of volumetric solutions. Throughout the book are numer-

ous problems, and the answers to these, together with useful tables, are found in the appendix. C. E. WATERS.

MILK, ITS PRODUCTION AND USES, WITH CHAPTERS ON DAIRY FARMING, THE DISEASES OF CATTLE, AND ON THE HYGIENE AND CONTROL OF SUPPLIES. By EDWARD F. WILLOUGHBY, M.D., D.P.H. London: Charles Griffin & Co. Philadelphia: J. B. Lippincott Co. 1904. 12 + 259 pp. Price, $2.00.

The general scope of this book and the object of the author are well indicated by the following portion of the preface: "Though the whole of the chapters will appeal equally to no man save, perhaps, the medical officer of health of a county, it would be well if every farmer and dairyman knew the ways and means by which milk may become a factor in the spread of disease, and had a rational conception of the nature of milk analysis. The analyst would be better able to draw sound conclusions from his estimations, if he understood the influence of breed, food and season on the composition of milk, and in this, as in so many subjects, the medical man is bound to endeavor to 'know something of everything.'" The book contains little that appeals directly to chemists. The treatment of the subject of milk analysis is far from complete. In stating the average composition of cows' milk, the author gives the fat as 3.8 per cent. and casein and albumin as 3.7 per cent. The relation of fat and proteids indicated by this average analysis does not represent American results, since in the United States milk containing 3.8 per cent. of fat would average more nearly 3.2 per cent. of proteids. Then the average analysis stated by the author gives casein as 3.3 per cent. and albumin 0.4 per cent. The normal relation should be nearer 2.50 per cent. of casein and 0.7 per cent. of albumin. The book appears, on the whole, to be carefully written and will be found of special value to veterinarians and health officers.

L. L. VAN SLYKE.

METHODS OF CHEMICAL CONTROL IN CANE-SUGAR FACTORIES. By H. C. PRINSEN GEERLIGS, Director of the West Java Sugar Experiment Station. Published by Norman Rodger, Altrincham (Manchester), Price, 3s. 6d. net.

This little work of 90 pages is in large part the English version of a bulletin of methods issued originally in Dutch by the West Java Sugar Experiment Station. The English text first appeared in 1904 in the *International Sugar Journal* and is now

reprinted in book form, with the addition of many tables and plans not hitherto published. The name of Prinsen Geerligs certainly needs no introduction to those interested in cane-sugar, and the many friends of his previous work upon the "Sugar Cane in Java" will welcome this new book, previously inaccessible to many in the original Dutch.

The first part of the book gives in condensed form methods for the analysis of cane, bagasse, juices, press-cakes, masse-cuites, molasses, and sugars, together with a chapter upon calculations and interpretation of results. The remainder of the text deals with the reporting of results and the equipment of the sugar-house laboratory.

A complete set of tables for laboratory use and a model of books and forms for the sugar-house are given in the second half of the book.

Several of the methods described are open to some criticism, especially that of sampling juices, given as follows (p. 8.): "During grinding small quantities of juice are continually taken from the gutters with a 10 cc. measure." Such a method is now obsolete in the best American practice, having been discarded for some form of continuous sampler, which requires no attention and gives a more uniform sample of juice.

The book is written entirely from a Java standpoint and local conditions in other cane-producing countries do not render all the methods described universally applicable. The method, for example, of determining the point of maturity of the cane-field (p. 4) would be valueless in Louisiana. But apart from such minor criticisms this new publication will prove of great value to the sugar-house chemist, even if its directions be not followed in every particular.

C. A. BROWNE, JR.

SELECT METHODS OF FOOD ANALYSIS. By HENRY LEFFMANN and WILLIAM BEAM. Philadelphia: P. Blakiston & Co. Second Edition. 1905. 596 pp. Price, $2.50.

During the last five years great progress has been made in the field of food chemistry, and many valuable methods and results of analyses have been published. The trend of modern investigation has been largely along the line of simplifying processes and suggesting "short cuts" to methods too complicated and intricate to be of practical value. This newer material has been well digested by the authors in the second edition of their book, re-

placing much that was obsolete in the first edition. The entire book has been rewritten, to record the latest results of the work of the State and Government food laboratories.

Recent problems, such as the detection of palm oil in oleomargarine, the identification of egg substitutes, and the modern examination of maple products, are exceedingly well treated. The new Government standards of purity for food products, so far as adopted, have been included.

No mention is made of the Babcock process of fat determination in milk, a noticeable omission, in view of the importance and extensive laboratory use of the process. More frequent references to original sources of information might perhaps be helpful to those who wish to further investigate data or methods.

The work as revised is a convenient and excellent handbook in condensed form for the laboratory worker, and should be on the shelves of every food chemist. ALBERT E. LEACH.

THE USE OF COAL TAR COLORS IN FOOD PRODUCTS. By HUGO LIEBER. New York: H. Lieber & Co. 1904. 150 pp.

The main portion of this book is devoted to physiological experiments showing the effect of coal-tar colors on dogs and rabbits, applying the colors both hypodermically and through the stomach with the food. It is largely a translation of Dr. Theodore Weyl's *Die Theerfarben*, and it would seem as if this fact should be made apparent on the title-page or in the preface, yet such is not the case. True, the author in one place in the text mentions that he is copying reports of Weyl and others, but the extent of his indebtedness is not apparent to the reader, who would naturally assume most of the subject-matter to be the work of Lieber rather than of Weyl.

It should be said that an excellent authorized translation by Leffmann of this same book of Weyl was published in 1892 entitled "The Sanitary Relations of the Coal Tar Colors," covering the same ground.

In addition to the physiological experiments, Lieber gives an interesting summary of the laws in foreign countries relating to coal-tar colors in foods. He urges the necessity of forcing dealers in colors intended for food products to sell such colors only as have been demonstrated to be harmless, and that manufacturers of food products should use more care in the choice of their colors.

ALBERT E. LEACH.

QUANTITATIVE METALLURGICAL ANALYSIS. SELECTED METHODS FOR CHEMICAL ANALYSIS OF ORES, SLAGS, COAL, PIG IRON AND STEEL. Arranged by CHARLES FREDERICK SIDENER, B.S., Assistant Professor of Chemistry, University of Minnesota. Minneapolis: The H. W. Wilson Co. 1904. 58 pp. Price, $1.00.

This little manual contains, in compact form, procedures for the analysis of the different classes of materials indicated in the sub-title above. They have presumably been thus brought together for the convenience of the compiler's pupils. The methods selected are generally of recognized merit, and are in nearly all cases, given in careful detail. They are accompanied by references to text-book or journal literature. H. P. T.

VERFLÜSSIGTES AMMONIAK ALS LÖSUNGSMITTEL. Materialien über die chemischen Eigenschaften des verflüssigten Ammoniak-gases gesammelt. Von J. BRONN. Berlin: Julius Springer. 1905. 8vo., xii + 252 pp. Price, 6 marks.

Convinced that there is much promise of commercial use for a liquid exhibiting such valuable solvent properties as ammonia has been shown to possess, the author has been led to collect the widely scattered material bearing on the subject and to give in the little volume before us as complete an account as possible of our present knowledge of the properties of liquid ammonia. The contents of the volume will be sufficiently indicated by an enumeration of the headings of its seven chapters. 1. The Physical Properties of Liquid Ammonia. Transportation and Methods of Testing the Liquid. Experimental Technique. 2. Deliquescent Action of Ammonia Gas and the Absorption of Ammonia by Various Substances. 3. Liquid Ammonia as a Solvent for Metals and Other Substances (older investigations). 4. Metal Ammonias and Metallic Amides. 5. Liquid Ammonia as a Solvent (recent investigations). 6. Metathetic Reactions in Liquid Ammonia. 7. Physico-Chemical Investigations with Liquid Ammonia. Various Tables.

The work of the author has been carefully done and the result is a book which gives not only a good account of the investigations which have been carried out in this field during the past forty years, but which also serves as a complete bibliography of the subject. The book is remarkably free from errors of all kinds, but very few minor mis-statements having been noticed by the reviewer in a rather careful perusal of the book.

E. C. F.

RECENT PUBLICATIONS.

GAS PRODUCERS FOR POWER PURPOSES. By W. A. Tookey. New York: Spon & Chamberlain. 1905. 141 pp. 50 cents.

OUTLINES OF INDUSTRIAL CHEMISTRY: A TEXT-BOOK FOR STUDENTS. By Frank Hall Thorp. Second edition, revised and enlarged, and including a Chapter on Metallurgy by C. D. Demond. New York: Macmillan. 1905. 26+618 pp. $3.50 net.

GUM-BICHROMATE PROCESS. By J. C. Richards. London: Iliffe. 1905. 120 pp. 2/6.

THERMODYNAMIK TECHNISCHER GASREAKTIONEN. 7 Vorlesungen. Von F. Haber. München: Oldenbourg. 1905. 15+296 pp. Marks 10.

DIE ENTWICKELUNG DER SPECTROCHEMIE. Von Julius Wilhelm Brühl. Berlin: J. Springer. 1905. 37 pp. One Mark.

ANLEITUNG ZUR QUALITATIVEN ANALYSE DER ELEKTROPOSITIVEN ELEMENTE (KATHIONEN). (1. Bl.) Von Rudolfo Fritsch. Wien: F. Deuticke. 1905. One mark.

ANALYSE DER DROGENPULVER. 11. Lfg. Von L. Koch. Leipzig: Borntraeger. nn. Marks 3.50.

ERGEBNISSE UND PROBLEME DER ELEKTRONENTHEORIE. Von H. A. Lorentz. Berlin: J. Springer. 1905. 62 pp. M. 1.50.

DIE UNTERSUCHUNG DER NAHRUNGS- UND GENUSSMITTEL SOWIE EINIGER GEBRAUCHSGEGENSTÄNDE. LEITFADEN FÜR DEN UNTERRICHT UND HILFSBUCH FÜR DIE AUSÜBG. DER NAHRUNGSMITTEL KONTROLLE IM LABORATORIUM. 2-te. vollständig umgearb. und verm. Auflage. Von M. Mansfeld. Wien: F. Deuticke. 1905. 16+243 pp. Marks 4.

DIE ELEKTROCHEMIE DER ORGANISCHEN VERBINDUNGEN. UNSERE KENTNISSE IN DER ELEKTROLYSE UND ELEKTROSYNTHESE ORGANISCHER VERBINDUNGEN. Von Walther Löb. Third edition. Halle: W. Knapp. 1905. 7+320 pp. Marks 9.

HANDBUCH DER ANORGANISCHEN CHEMIE. Von Gmelin und Kraut. Seventh edition. Ed. by A. Hilger und C. Friedheim (In ca. 70 Lfgn). 1 Lfg. (1.Bd. pp. 1-60). Heidelberg: C. Winter. 1905. Marks 1.80.

TREATISE ON CHEMISTRY. By Sir H. E. Roscoe and C. Schorlemmer. Vol. 1, Non-Metallic Elements. New edition completely revised by Sir H. E. Roscoe, assisted by Drs. H. G. Colman and A. Harden. London: Macmillan. 1905. 944 pp. 21/net.

LEAD POISONING IN EARTHENWARE AND CHINA WORKS. London: Wyman. 1905. 11/2d.

SYSTEMATIC COURSE OF PRACTICAL ORGANIC CHEMISTRY. By L. G. Radcliffe and F. S. Sinnatt. London: Longmans. 1905. 276 pp. 4/6.

SELECTED METHODS OF FOOD ANALYSIS. By H. Leffmann. Philadelphia: P. Blakiston's Son & Co. 1905. 396 pp. $2.50 net.

SYNTHETIC DYE-STUFFS AND INTERMEDIATE PRODUCTS FROM WHICH THEY ARE DERIVED. By J. C. Cain and J. Field Thorpe. London: Griffin. 1905. 422 pp. 16/.

FARBENFABRIKATION. 2-10. Lfg. Von R. Zerr und G. Rübencamp. Dresden: Steinkopff & Springer. One mark.

FABRICATION ET RAFFINAGE DES HUILES VÉGÉTALES. Par J. Fritsch. Paris: H. Desforges. 600 pp. 12 francs.

CONTRIBUTION A L'ÉTUDE DES APPLICATIONS THÉRAPEUTIQUES DES OXYDASES ET DES MÉTAUX FERMENTS. Par P. Sée. Paris: O. Doin. 540 pp. 12 francs.

TRAITÉ PRATIQUE DE CALORIMETRIQUE CHIMIQUE. Par M. Berthelot. Paris: Gauthier-Villars. 6 francs.

APPRETUR DER BAUMWOLLGEWEBE. ANLEITUNG DIE WEISSEN, GEFÄRBTEN UND BEDRUCKTEN BAUMWOLLGEWEBE ZU APPRETIEREN. Von Jos. Dépierre. 2 Aufl. nach der 3-te. französ. Wien: Gerold. 1905. 4+418 pp. M. 40.

OUTLINES OF INORGANIC CHEMISTRY. By Frank Austin Gooch and C. F. Walker. New York: Macmillan. 1905. $1.75 net.

HANDBUCH DER SPECTROSCOPIE. Von. H. Kayser. Leipzig: Hirzel. 1905. 3 Bd. M. 38.

KURZES LEHRBUCH DER CHEMIE. ANORGANISCHE CHEMIE. Von F. Krafft. 5 Aufl. Wien: Deuticke. 1904. 14+525 pp. M. 9. ORGANISCHE CHEMIE. 4 Aufl. 1905. M. 15.

PRACTICAL METHODS OF ELECTROCHEMISTRY. By F. Mollwo Perkin. New York: Longmans. 1905. $1.60.

POISONOUS PLANTS OF ALL COUNTRIES: ACTIVE CHEMICAL PRINCIPLES WHICH THEY CONTAIN: TOXIC SYMPTOMS PRODUCED BY EACH GROUP. By A. B. Smith. Simpkin. 1905. 104 pp. 2/6.

MANUEL PRATIQUE POUR L'EXAMEN CHIMIQUE DES URINES. Par R. Etienne. Paris: A. Maloine. 70 pp. 2.50 francs.

LES NOUVEAUTÉS CHIMIQUES POUR 1905. Par Poudenc. Paris: J. B. Baillière et fils. 342 pp. 4 francs.

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DIE PRAXIS DES ORGANISCHEN CHEMIKERS. Von Ludwig Gattermann. Siebente Auflage. Leipzig : Veit & Co. 1905. 12+352 pp. Marks 7.50.

ÜBER DIE ANWENDUNG DES SALZSAUREN HYDROXYLAMINS IN DER QUANTITATIVEN ANALYSE. Von Pet. Hasenclever. Wiesbaden : C. W. Kreidel. 1905. 34 pp. Marks, 80.

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HINTS ON PAINTING STRUCTURAL STEEL AND NOTES ON PROMINENT PAINT MATERIALS : A HANDBOOK FOR PAINT-USERS. By Houston Lowe. Fourth enlarged edition. Dayton, Ohio : Lowe Brothers. 1905. Cloth, $1.00. Paper, 50 cents.

LE FOUR ÉLECTRIQUE. SON ORIGINE, SES TRANSFORMATIONS ET APPLICATIONS. First fasc. Par A. Minet. Paris : A. Hermann. 76 pp. 5 francs.

ELDERS' APPEAL CASES UNDER THE FOOD AND DRUGS ACT, WITH APPENDIX OF CASES TO 1905. London : Butterworth. 1905. 3/6.

REPORT BY MEDICAL INSPECTOR OF FACTORIES ON MANUFACTURE OF PAINTS AND COLOURS CONTAINING LEAD. London : Wyman. 1905. $11\frac{1}{2}$d.

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